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(54) **EXHAUST PURIFICATION SYSTEM OF INTERNAL COMBUSTION ENGINE**

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(56) **References Cited**

U.S. PATENT DOCUMENTS

5,052,178 A 10/1991 Clerc et al.
5,057,483 A 10/1991 Wan
(Continued)

FOREIGN PATENT DOCUMENTS

CN 101454081 A 6/2009
CN 101600860 A 12/2009
(Continued)

OTHER PUBLICATIONS

Office Action dated Oct. 24, 2013 issued in U.S. Appl. No. 13/255,710.
(Continued)

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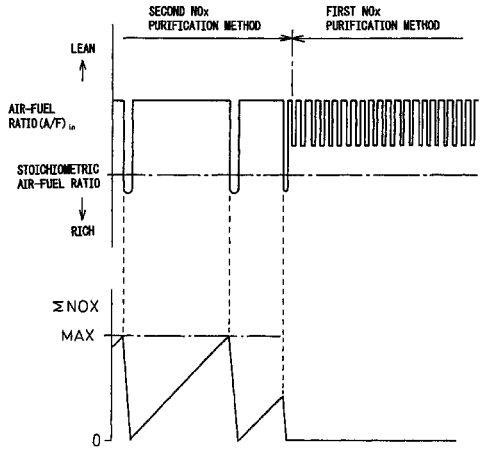
(57) **ABSTRACT**

A method of purifying NO_X contained in exhaust gas, the method including a first NO_X purification method and a second NO_X purification method, wherein the first NO_X purification method and the second NO_X purification method include injecting hydrocarbons into an exhaust gas passage at predetermined feed intervals, wherein in the first method, the injected hydrocarbons are partially oxidized and an air-fuel ratio flowing into an exhaust purification catalyst is lean, and in the second method, the injection of the hydrocarbons occurs at intervals longer than the predetermined feed intervals in the first method, and an air-fuel ratio is switched from lean to rich.

19 Claims, 17 Drawing Sheets



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(56) **References Cited**

U.S. PATENT DOCUMENTS

5,075,274	A	12/1991	Kiyohide et al.
5,402,641	A	4/1995	Katoh et al.
5,882,607	A	3/1999	Miyadera et al.
6,109,024	A	8/2000	Kinugasa et al.
6,327,851	B1	12/2001	Bouchez et al.
6,413,483	B1	7/2002	Brisley et al.
6,477,834	B1	11/2002	Asanuma et al.
6,667,018	B2	12/2003	Noda et al.
6,813,882	B2	11/2004	Hepburn et al.
6,854,264	B2	2/2005	Elwart et al.
6,877,311	B2	4/2005	Uchida
6,983,589	B2	1/2006	Lewis et al.
7,063,642	B1	6/2006	Hu et al.
7,073,325	B2	7/2006	Nakatani et al.
7,082,753	B2	8/2006	Dalla Betta et al.
7,111,456	B2	9/2006	Yoshida et al.
7,137,379	B2	11/2006	Sasaki et al.
7,146,800	B2	12/2006	Toshioka et al.
7,165,393	B2	1/2007	Betta et al.
7,299,625	B2	11/2007	Uchida et al.
7,332,135	B2	2/2008	Gandhi et al.
7,412,823	B2	8/2008	Reuter et al.
7,454,900	B2	11/2008	Hayashi
7,484,504	B2	2/2009	Kato et al.
7,506,502	B2	3/2009	Nakano et al.
7,549,284	B2	6/2009	Iihoshi et al.
7,703,275	B2	4/2010	Asanuma et al.
7,707,821	B1	5/2010	Legare
7,861,516	B2	1/2011	Allansson et al.
8,099,950	B2	1/2012	Kojima et al.
8,215,101	B2	7/2012	Tsujimoto et al.
8,261,532	B2	9/2012	Fukuda et al.
8,281,569	B2	10/2012	Handa et al.
8,434,296	B2	5/2013	Wada et al.
8,572,950	B2	11/2013	Bisaiji et al.
8,656,706	B2	2/2014	Umemoto et al.
8,671,667	B2	3/2014	Bisaiji et al.
8,679,410	B2	3/2014	Umemoto et al.
8,689,543	B2	4/2014	Numata et al.
8,695,325	B2	4/2014	Bisaiji et al.
2001/0052232	A1	12/2001	Hoffmann et al.
2002/0029564	A1	3/2002	Roth et al.
2002/0053202	A1	5/2002	Akama et al.
2003/0010020	A1	1/2003	Taga et al.
2003/0040432	A1	2/2003	Beall et al.
2003/0101713	A1	6/2003	Dalla Betta et al.
2004/0045285	A1	3/2004	Penetrante et al.
2004/0050037	A1	3/2004	Betta et al.
2004/0055285	A1	3/2004	Rohr et al.
2004/0154288	A1	8/2004	Okada et al.
2004/0175305	A1	9/2004	Nakanishi et al.
2004/0187477	A1	9/2004	Okugawa et al.
2005/0135977	A1	6/2005	Park et al.
2005/0147541	A1	7/2005	Ajisaka et al.
2006/0053778	A1	3/2006	Asanuma et al.
2006/0107657	A1	5/2006	Bernler et al.
2006/0153761	A1	7/2006	Bandl-Konrad et al.
2006/0286012	A1	12/2006	Socha et al.
2007/0016357	A1	1/2007	Nakagawa et al.
2007/0028601	A1	2/2007	Duvinage et al.
2007/0059223	A1	3/2007	Golunski et al.
2007/0089403	A1	4/2007	Pfeifer et al.
2007/0125073	A1	6/2007	Reuter et al.
2007/0151232	A1	7/2007	Dalla Betta et al.
2008/0022662	A1	1/2008	Yan
2008/0053073	A1	3/2008	Kalyanaraman et al.
2008/0102010	A1	5/2008	Bruck et al.
2008/0120963	A1	5/2008	Morita et al.
2008/0148711	A1	6/2008	Takubo
2008/0154476	A1	6/2008	Takubo
2008/0196398	A1	8/2008	Yan
2008/0223020	A1	9/2008	Yoshida et al.
2008/0276602	A1	11/2008	McCabe et al.
2009/0000277	A1	1/2009	Yoshida et al.
2009/0049824	A1	2/2009	Kojima et al.
2009/0049825	A1	2/2009	Ohashi
2009/0049826	A1	2/2009	Toshioka et al.
2009/0077948	A1	3/2009	Mondori et al.
2009/0084091	A1	4/2009	Tsujimoto et al.
2009/0118121	A1	5/2009	Sarai
2009/0120072	A1	5/2009	Dalla Betta et al.
2009/0151332	A1	6/2009	Toshioka et al.
2009/0191108	A1	7/2009	Blanchard et al.
2009/0196811	A1	8/2009	Yamashita et al.
2009/0229251	A1	9/2009	Kadowaki
2009/0249768	A1	10/2009	Asanuma et al.
2009/0266057	A1	10/2009	Tsujimoto et al.
2009/0282809	A1	11/2009	Toshioka
2009/0288393	A1	11/2009	Matsuno et al.
2009/0313970	A1	12/2009	Iida
2010/0005873	A1	1/2010	Katoh et al.
2010/0055012	A1	3/2010	Grisstede et al.
2010/0107613	A1	5/2010	Masuda et al.
2010/0115923	A1	5/2010	Tsujimoto et al.
2010/0126148	A1	5/2010	Morishima et al.
2010/0132356	A1	6/2010	Lee
2010/0154387	A1	6/2010	Shibata et al.
2010/0233051	A1	9/2010	Grisstede et al.
2010/0236224	A1	9/2010	Kumar et al.
2010/0242459	A1	9/2010	Tsujimoto et al.
2011/0041486	A1	2/2011	Kato et al.
2011/0047984	A1	3/2011	Lee et al.
2011/0047988	A1	3/2011	Lewis et al.
2011/0113754	A1	5/2011	Kohara et al.
2011/0120100	A1	5/2011	Yin et al.
2011/0131952	A1	6/2011	Onodera et al.
2011/0173950	A1	7/2011	Wan et al.
2011/0209459	A1	9/2011	Hancu et al.
2012/0122660	A1	5/2012	Andersen et al.
2012/0124967	A1	5/2012	Yang et al.
2012/0124971	A1	5/2012	Bisaiji et al.
2012/0131908	A1	5/2012	Bisaiji et al.
2013/0000284	A1	1/2013	Bisaiji et al.
2013/0011302	A1	1/2013	Bisaiji et al.
2013/0022512	A1	1/2013	Bisaiji et al.

(56) **References Cited**

U.S. PATENT DOCUMENTS

FOREIGN PATENT DOCUMENTS

EP	1 033 479 A2	9/2000
EP	1 273 337 A1	1/2003
EP	1 371 415 A1	12/2003
EP	1 519 015 A2	3/2005
EP	1544429 A1	6/2005
EP	1 710 407 A1	10/2006
EP	1 793 099 A1	6/2007
EP	1 911 506 A1	4/2008
EP	1 936 164 A1	6/2008
EP	1965 048 A1	9/2008
EP	2 063 078 A1	5/2009
EP	2 149 684 A1	2/2010
EP	2 239 432	10/2010
EP	2 460 989 A1	6/2012
JP	A-04-200637	7/1992
JP	H-08-117601	5/1996
JP	A-09-004437	1/1997
JP	A-09-220440	8/1997
JP	A-11-30117	2/1999
JP	A-11-062559	3/1999
JP	A-11-081994	3/1999
JP	A-2000-257419	9/2000
JP	A-2002-188429	7/2002
JP	A-2004-016850	1/2004
JP	A-2004-36543	2/2004
JP	A-2004-216224	8/2004
JP	A-2004-290965	10/2004
JP	A-2004-308526	11/2004
JP	A-2004-316458	11/2004
JP	A-2005-61340	3/2005
JP	A-2005-113801	4/2005
JP	A-2005-171853	6/2005
JP	A-2005-177738	7/2005
JP	A-2006-501390	1/2006
JP	A-2006-512529	4/2006
JP	A-2006-342700	12/2006
JP	A-2007-064167	3/2007
JP	A-2007-514090	5/2007
JP	A-2007-514104	5/2007
JP	A-2007-154794	6/2007
JP	B2-3969450	6/2007
JP	A-2007-278120	10/2007
JP	A-2008-002451	1/2008
JP	A-2008-19760	1/2008
JP	A-2008-69769	3/2008
JP	A-2008-231926	10/2008
JP	A-2008-232003	10/2008
JP	A-2008-255858	10/2008
JP	A-2008-267178	11/2008
JP	A-2008-267217	11/2008
JP	A-2008-286186	11/2008
JP	A-2008-543559	12/2008
JP	A-2009-30560	2/2009
JP	A-2009-112967	5/2009
JP	A-2009-114879	5/2009
JP	A-2009-156067	7/2009
JP	A-2009-165922	7/2009
JP	A-2009-167973	7/2009
JP	A-2009-168031	7/2009
JP	A-2009-191823	8/2009
JP	A-2009-221939	10/2009
JP	A-2009-226349	10/2009
JP	A-2009-243362	10/2009
JP	A-2009-275631	11/2009
JP	A-2009-275666	11/2009
JP	A-2010-012459	1/2010
JP	A-2010-048134	3/2010
JP	A-2011-190803	9/2011
JP	B1-4868097	2/2012
WO	WO 2005/059324	6/2005
WO	WO 2006/131825	12/2006
WO	WO 2007/026229	3/2007
WO	WO 2007/141638	12/2007
WO	WO 2008/007810	1/2008
WO	WO 2008/012653 A2	1/2008
WO	WO 2009/016822	2/2009
WO	WO 2009/056958	5/2009
WO	WO 2009/082035 A1	7/2009
WO	WO 2011/114499	9/2011
WO	WO 2011/114501	9/2011
WO	WO 2011/118044	9/2011

OTHER PUBLICATIONS

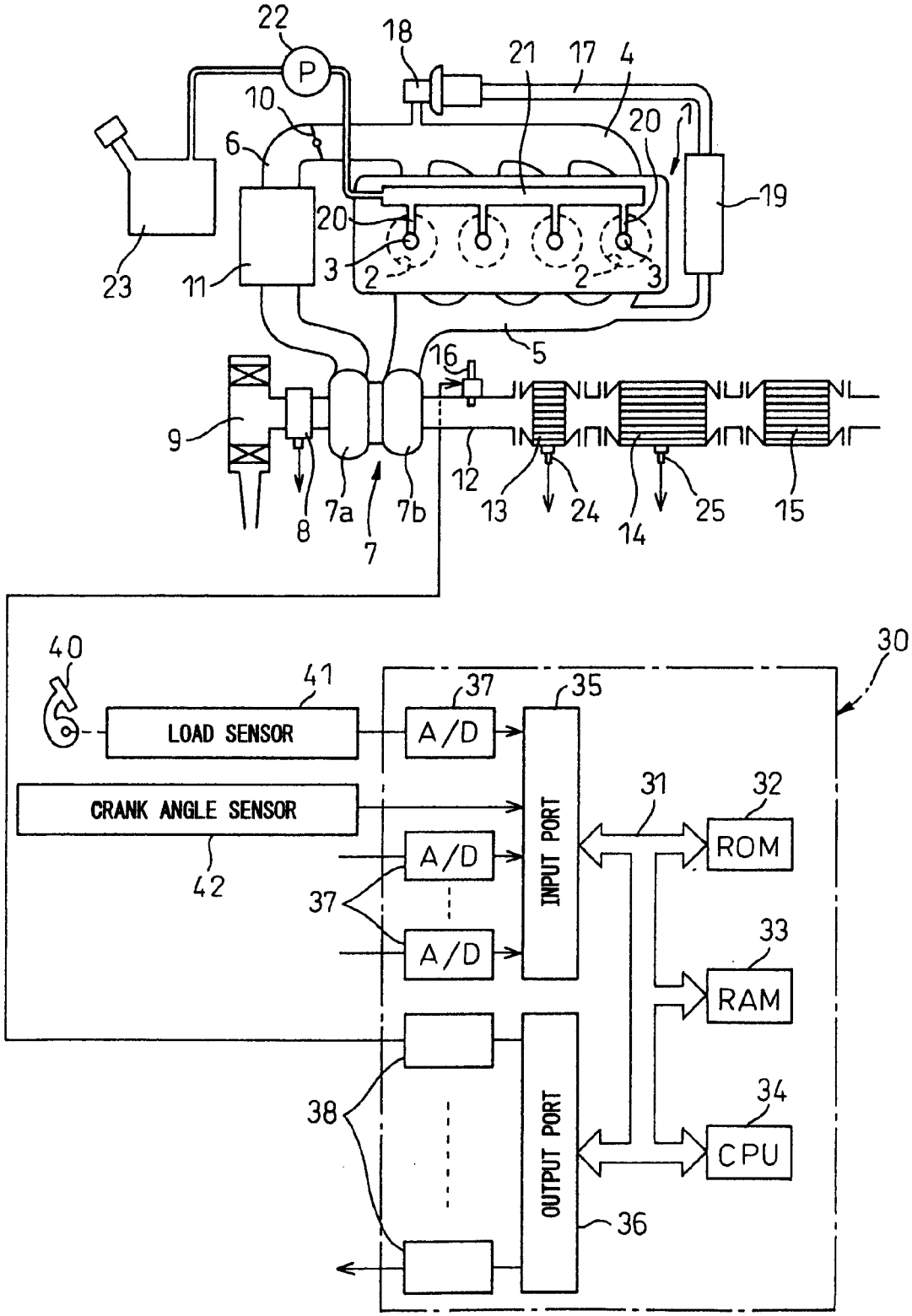
Office Action dated Dec. 20, 2013 issued in U.S. Appl. No. 13/264,230.
Aug. 13, 2013 International Preliminary Report on Patentability issued in International Patent Application No. PCT/JP2011/053429 (with translation).
Aug. 8, 2013 Office Action issued in U.S. Appl. No. 13/258,483.
Feb. 6, 2014 Corrected Notice of Allowability issued in U.S. Appl. No. 13/202,694.
Dec. 21, 2010 International Search Report issued in International Patent Application No. PCT/JP2010/065449.
Dec. 27, 2011 International Search Report issued in International Patent Application No. PCT/JP2011/075618.
Jun. 15, 2010 International Search Report issued in International Patent Application No. PCT/JP2010/054730 (with translation).
Nov. 22, 2010 International Search Report issued in International Patent Application No. PCT/JP2010/065186.
Jan. 18, 2011 International Search Report issued in International Patent Application No. PCT/JP2010/067705.
Jan. 18, 2011 International Search Report issued in International Patent Application No. PCT/JP2010/067707.
Jan. 18, 2011 International Search Report issued in International Patent Application No, PCT/JP2010/068785.
Jul. 14, 2014 Office Action issued in U.S. Appl. No. 13/262,001.
Jul. 14, 2014 Office Action issued in U.S. Appl. No. 13/264,884.
Jun. 16, 2014 Office Action issued in U.S. Appl. No. 13/581,186,.
Jun. 18, 2014 Office Action issued in U.S. Appl. No. 13/582,909.
Jun. 19, 2014 Office Action issued in U.S. Appl. No. 13/264,594.
Jun. 21, 2011 International Search Report issued in International Patent Application No. PCT/JP2011/059880.
Jun. 23, 2014 Office Action issued in U.S. Appl. No. 13/262,858.
Jun. 26, 2014 Office Action issued in U.S. Appl. No. 13/580,000.
Jun. 29, 2010 International Search Report issued in International Patent Application No. PCT/JP2010/055303.
Mar. 15, 2011 International Search Report issued in International Patent Application No. PCT/JP2011/053429.
Mar. 22, 2011 International Search Report issued in International Patent Application No. PCT/JP2010/073645.
Mar. 22, 2011 International Search Report issued in International Patent Application No. PCT/JP2010/072299.
Mar. 8, 2011 International Search Report issued in International Patent Application No. PCT/JP2011/052969 (with translation).
May 17, 2011 International Search Report issued in International Patent Application No. PCT/JP2011/057264.
May 2, 2014 Office Action issued in U.S. Appl. No. 13/263,660.
Mar. 28, 2014 Notice of Allowance issued in U.S. Appl. No. 13/582,862.
Mar. 4, 2014 Notice of Allowance issued in U.S. Appl. No. 13/255,786.
Nov. 13, 2013 Notice of Allowance issued in U.S. Appl. No. 13/202,692.
Oct. 17, 2013 Notice of Allowance issued in U.S. Appl. No. 13/202,694.
Nov. 22, 2010 International Search Report issued in International Patent Application No. PCT/JP2010/065187.
Nov. 26, 2012 Office Action issued in U.S. Appl. No. 13/202,694.
Oct. 26, 2010 International Search Report issued in International Patent Application No. PCT/JP2010/063135.
Oct. 26, 2012 Office Action issued in U.S. Appl. No. 13/202,692.
Oct. 23, 2013 Office Action issued in U.S. Appl. No. 13/263,272.
Apr. 23, 2014 Office Action issued in U.S. Appl. No. 13/260,986.
Apr. 3, 2014 Office Action issued in U.S. Appl. No. 13/259,574.
Jul. 1, 2014 Office Action issued in U.S. Appl. No. 13/257,789.

(56) **References Cited**

OTHER PUBLICATIONS

Jul. 24, 2013 Office Action issued in U.S. Appl. No. 13/202,692.
May 7, 2014 Office Action issued in U.S. Appl. No. 13/264,062.
May 8, 2014 Office Action issued in U.S. Appl. No. 13/375,674.
U.S. Appl. No. 13/202,733 in the name of Bisaiji et al., filed Sep. 30, 2011.
U.S. Appl. No. 13/257,789 in the name of Nishioka et al., filed Oct. 14, 2011.
U.S. Appl. No. 13/258,483 in the name of Numata et al., filed Sep. 22, 2011.
U.S. Appl. No. 13/259,574 in the name of Tsukamoto et al., filed Sep. 23, 2011.
U.S. Appl. No. 13/259,885 in the name of Umemoto et al., filed Sep. 23, 2011.
U.S. Appl. No. 13/260,986 in the name of Watanabe et al., filed Sep. 29, 2011.
U.S. Appl. No. 13/263,272 in the name of Bisaiji et al., filed Oct. 6, 2011.
U.S. Appl. No. 13/263,660 in the name of Umemoto et al., filed Oct. 7, 2011.
U.S. Appl. No. 13/264,062 in the name of Watanabe et al., filed Oct. 12, 2011.
U.S. Appl. No. 13/264,594 in the name of Inoue et al., filed Oct. 14, 2011.
U.S. Appl. No. 13/264,884 in the name of Bisaiji et al., filed Oct. 17, 2011.
U.S. Appl. No. 13/375,674 in the name of Inoue et al., filed Dec. 1, 2011.
U.S. Appl. No. 13/578,148 in the name of Umemoto et al., filed Aug. 9, 2012.
U.S. Appl. No. 13/581,186 in the name of Kazuhiro Umemoto et al., filed Aug. 24, 2012.
U.S. Appl. No. 13/580,000 in the name of Bisaiji et al., filed Aug. 20, 2012.
U.S. Appl. No. 13/582,862 in the name of Uenishi et al., filed Sep. 5, 2012.
U.S. Appl. No. 13/582,909 in the name of Kazuhiro Umemoto et al., filed Sep. 5, 2012.
U.S. Appl. No. 13/202,694 in the name of Bisaiji et al., filed Aug. 22, 2011.
U.S. Appl. No. 14/108,113 in the name of Bisaiji et al., filed Dec. 16, 2013.
U.S. Appl. No. 14/152,629 in the name of Umemoto et al., filed Jan. 10, 2014.
U.S. Appl. No. 13/262,001 in the name of Inoue et al., filed Oct. 19, 2011.
Nov. 22, 2010 Written Opinion issued in International Patent Application No. PCT/JP2010/065186 (with translation).
Dec. 27, 2011 Written Opinion issued in International Patent Application No. PCT/JP2011/075618.
Aug. 6, 2014 Notice of Allowance issued in U.S. Appl. No. 13/259,574.
Nov. 27, 2013 Notice of Allowance issued in U.S. Appl. No. 13/258,483.
Oct. 4, 2013 Notice of Allowance issued in U.S. Appl. No. 13/259,885.
Jan. 17, 2013 Office Action issued in U.S. Appl. No. 13/202,733.
Jun. 15, 2010 International Search Report issued in International Application No. PCT/JP2010/054729.
Sep. 13, 2011 International Search Report issued in International Application No. PCT/JP2011/066628 (with Translation).
U.S. Appl. No. 13/502,210 in the name of Bisaiji, filed Apr. 16, 2012.
U.S. Appl. No. 13/499,211 in the name of Bisaiji et al., filed Mar. 29, 2012.
Jan. 22, 2014 Office Action issued in U.S. Appl. No. 13/499,211.
Sep. 18, 2014 Notice of Allowance issued in U.S. Appl. No. 13/255,710.
Oct. 2, 2014 Office Action issued in U.S. Appl. No. 13/582,862.
Jul. 9, 2013 Notice of Allowance issued in U.S. Appl. No. 13/255,774.
Dec. 9, 2013 Notice of Allowance issued in U.S. Appl. No. 13/262,506.
Dec. 27, 2013 Notice of Allowance issued in U.S. Appl. No. 13/502,210.
U.S. Appl. No. 13/262,506 in the name of Bisaiji et al., filed Sep. 30, 2011.
Dec. 22, 2014 Office Action issued in U.S. Appl. No. 13/264,230.
Office Action dated May 27, 2014 issued in U.S. Appl. No. 13/255,710.
Jun. 15, 2010 International Search Report issued in PCT/JP2010/054740 (with translation).
Jun. 15, 2010 Written Opinion issued in PCT/JP2010/054740 (with translation).
Jun. 20, 2012 Search Report issued in European Patent Application No. 10845966.0.
U.S. Appl. No. 13/255,774, filed Sep. 22, 2011 in the name of Bisaiji et al.
U.S. Appl. No. 13/255,710, filed Oct. 12, 2011 in the name of Bisaiji et al.
U.S. Appl. No. 13/262,858, filed Oct. 4, 2011 in the name of Bisaiji et al.
U.S. Appl. No. 13/264,230, filed Oct. 13, 2011 in the name of Bisaiji.
U.S. Appl. No. 13/202,692, filed Sep. 20, 2011 in the name of Umemoto et al.
Office Action dated May 15, 2013 issued in U.S. Appl. No. 13/202,694.
Jun. 15, 2010 International Search Report issued in International Patent Application No. PCT/JP2010/054731 (with translation).
Jun. 29, 2010 International Search Report issued in International Patent Application No. PCT/JP2010/056345.
Apr. 4, 2013 Office Action issued in U.S. Appl. No. 13/255,710.
Jun. 3, 2015 Office Action issued in U.S. Appl. No. 14/152,629.

Fig.1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LOAD SENSOR
A/D
CRANK ANGLE SENSOR
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A/D
INPUT PORT
31
32
ROM
33
RAM
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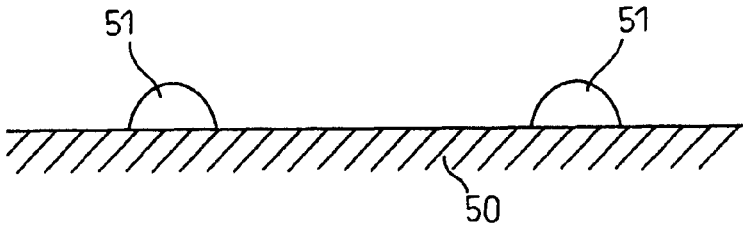
OUTPUT PORT
34
CPU
36

Fig. 2

(A)


51
51
50

(B)

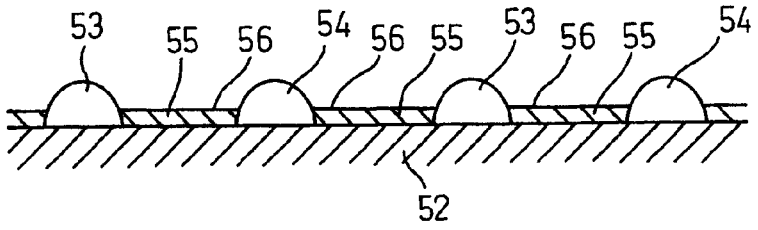

53
55
56
54
56
55
53
56
55
54
52

Fig. 3

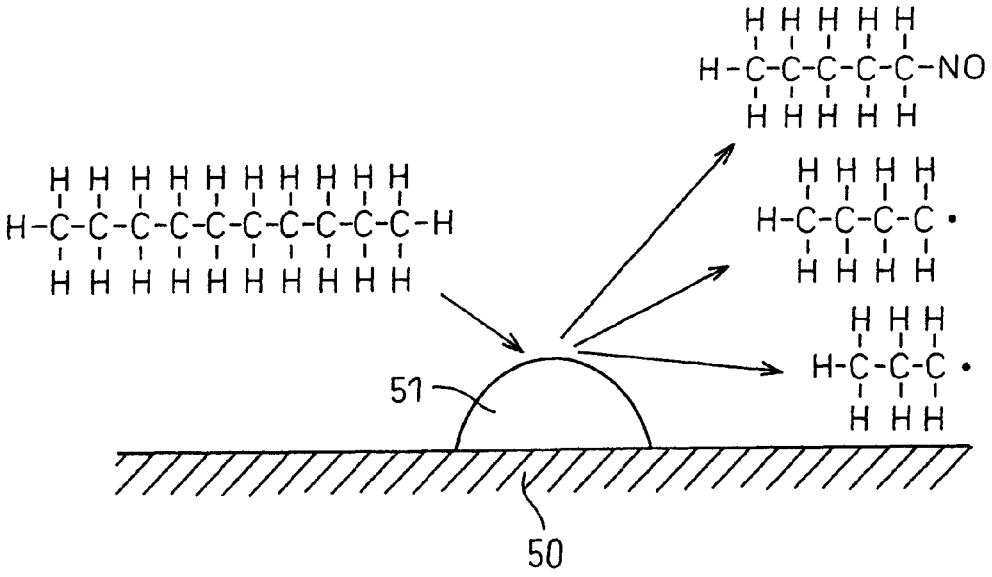

H H H H H
H-C-C-C-C-C-NO
H H H H H
H H H H H H H H H H
H-C-C-C-C-C-C-C-C-C-H
H H H H H H H H H H
H H H H
H-C-C-C-C •
H H H H
H H H
H-C-C-C •
H H H
51
50

Fig.4

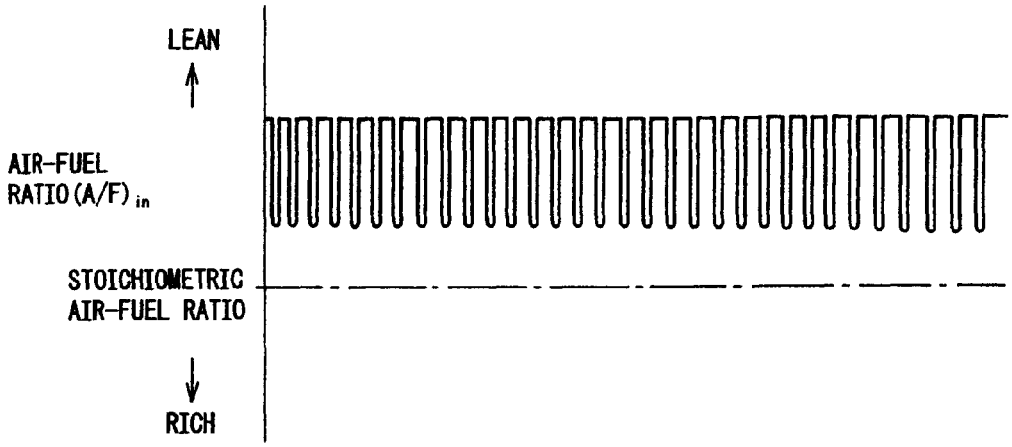

LEAN
AIR-FUEL RATIO (A/F) in
STOICHIOMETRIC AIR-FUEL RATIO
RICH

Fig.5

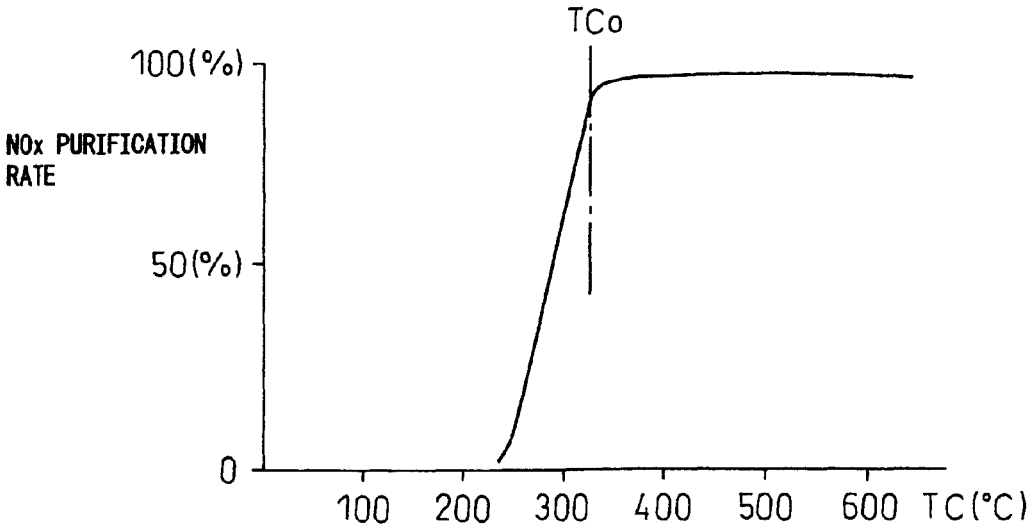
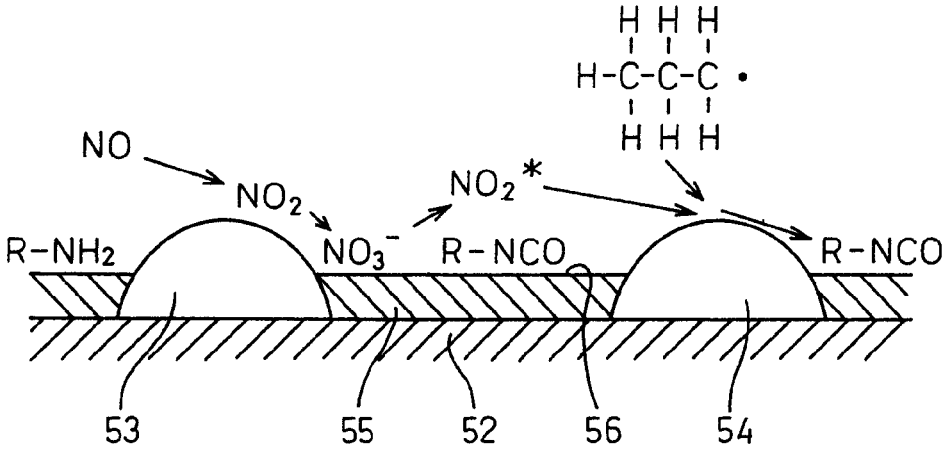

TCo
100(%)
NOx PURIFICATION RATE
50(%)
0
100
200
300
400
500
600
TC(°C)

Fig. 6

(A)


H H H
H-C-C-C •
H H H
NO
NO2
NO2*
R-NH2
NO3-
R-NCO
R-NCO
53
55
52
56
54

(B)

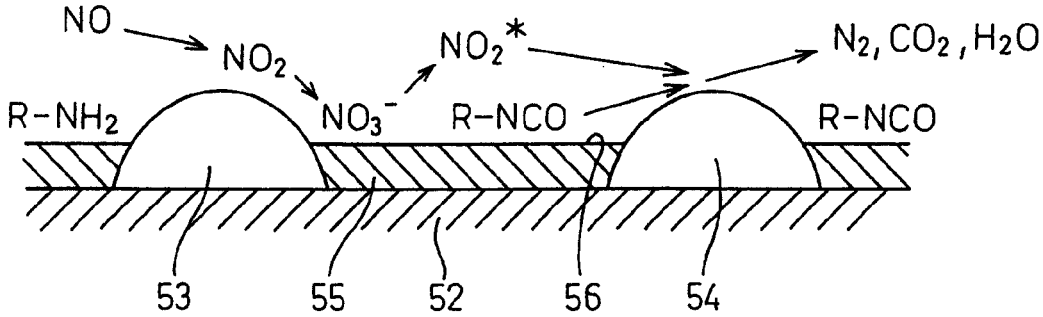
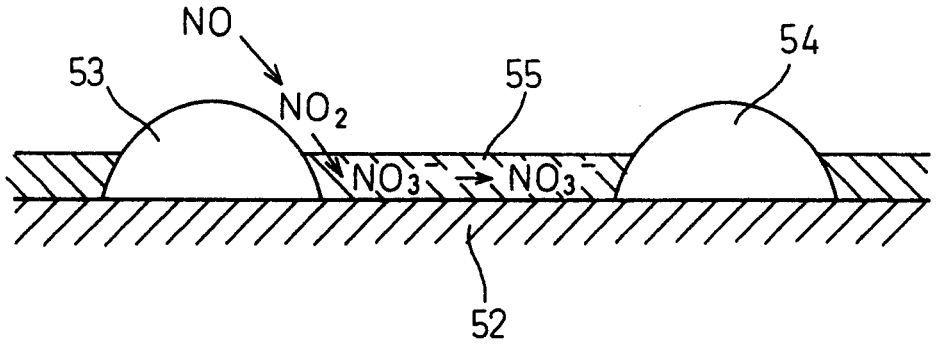

NO
NO2
NO2*
N2, CO2, H2O
R-NH2
NO3-
R-NCO
R-NCO
53
55
52
56
54

Fig.7

(A)



(B)

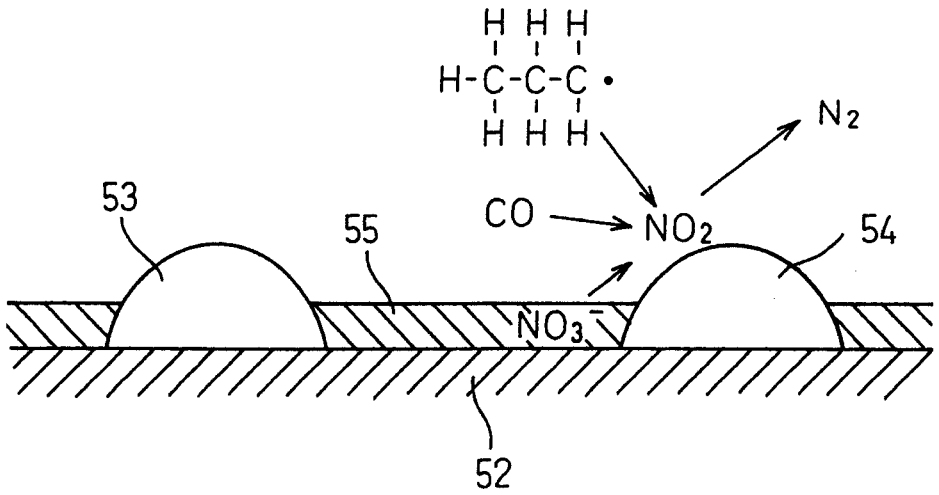


Fig.8

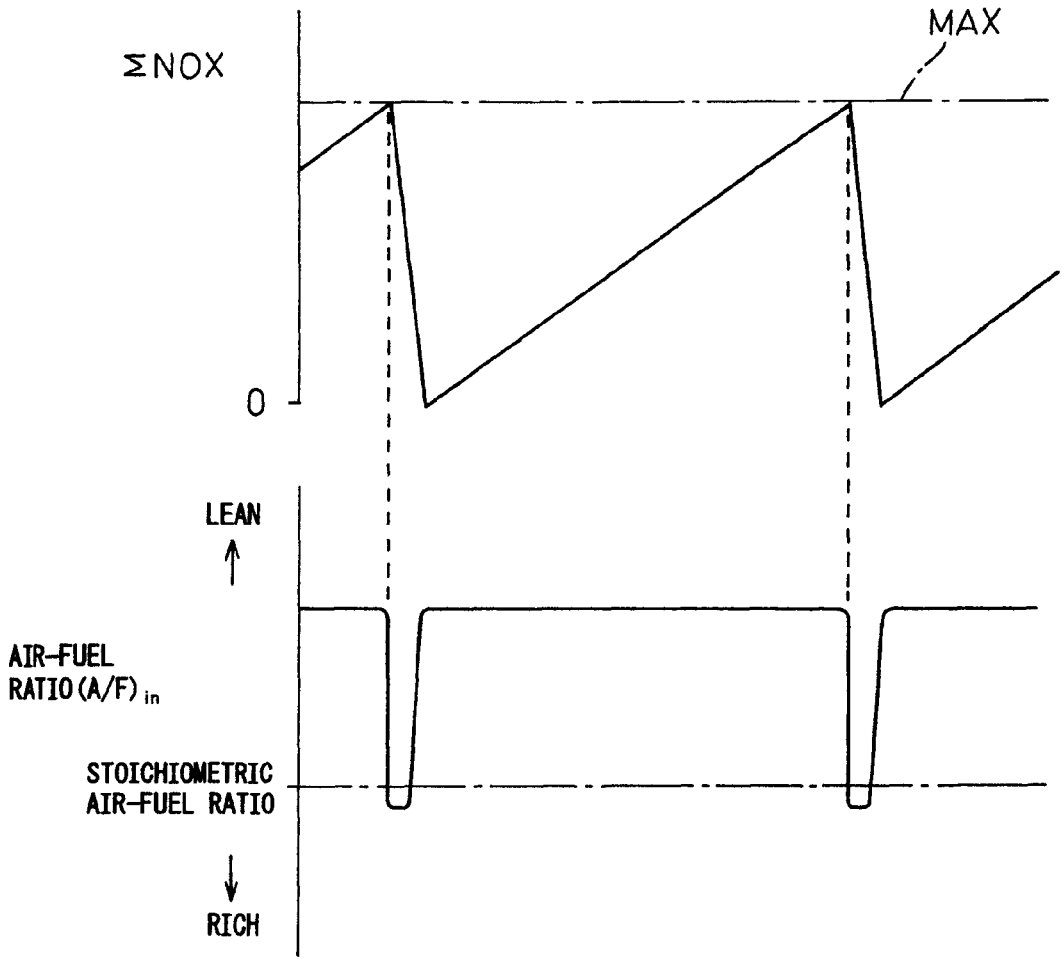

ΣNOX
MAX
0
LEAN
AIR-FUEL RATIO (A/F) in
STOICHIOMETRIC AIR-FUEL RATIO
RICH

Fig.9

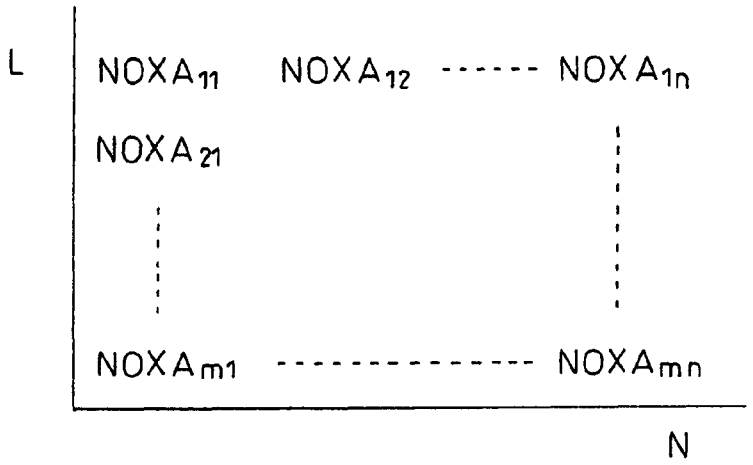

L
NOXA11
NOXA12
NOXA1n
NOXA21
NOXAm1
NOXAmn
N

Fig.10

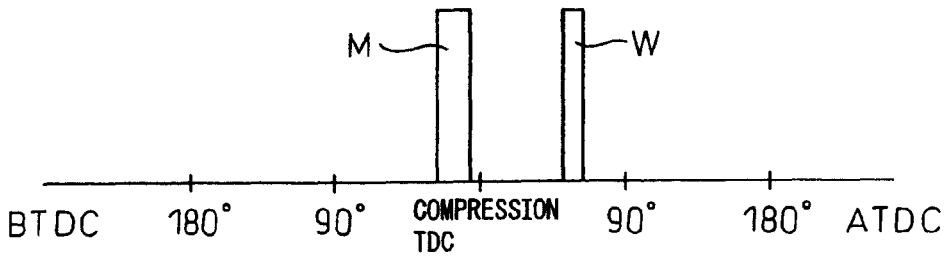

M
W
BTDC
180°
90°
COMPRESSION TDC
90°
180°
ATDC

Fig.11

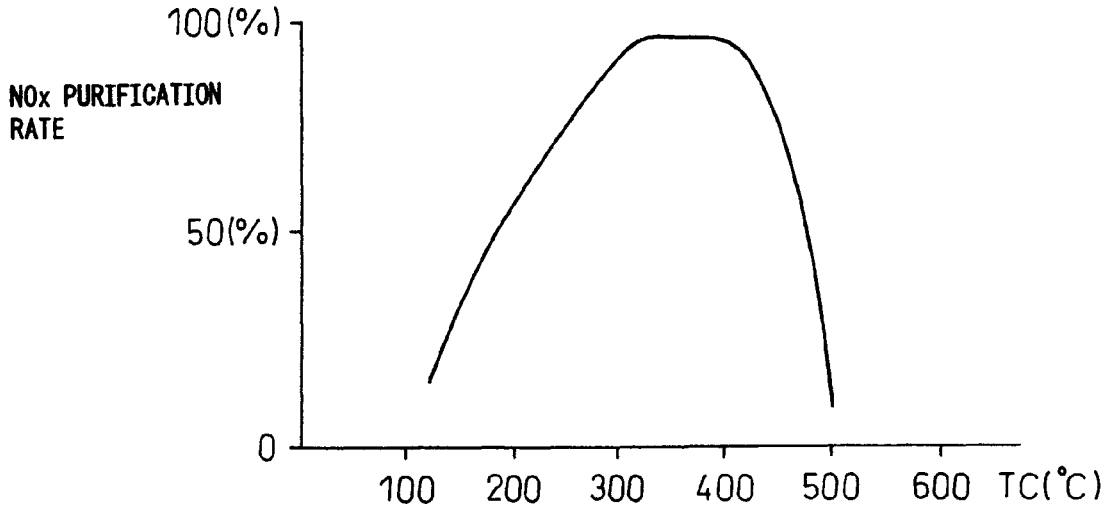
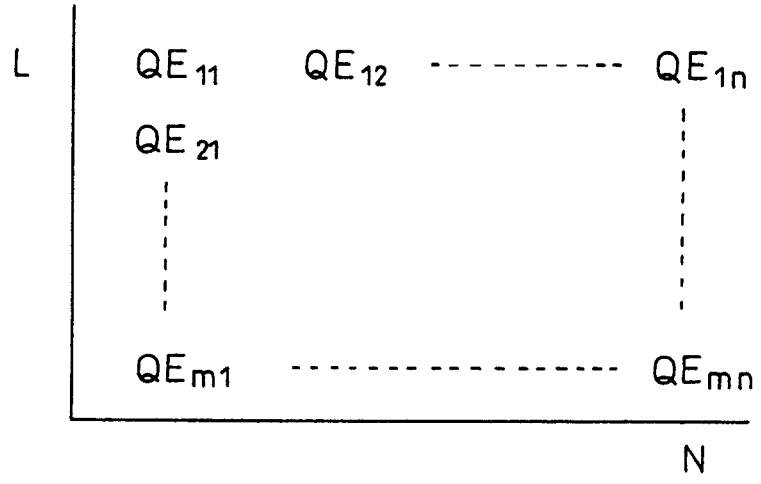


Fig.12

(A)



(B)

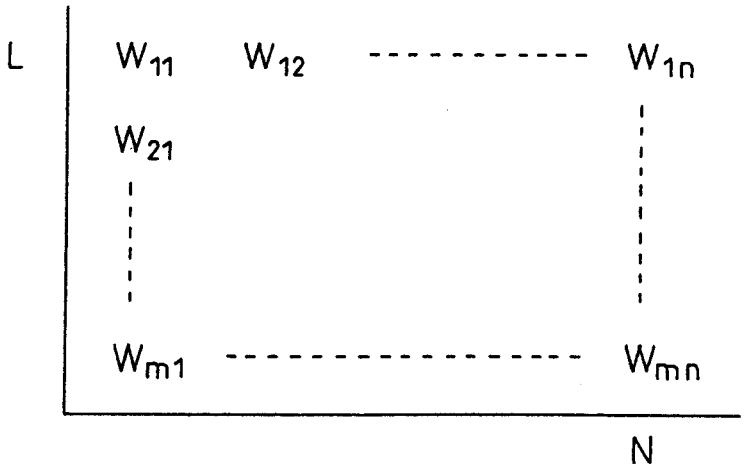
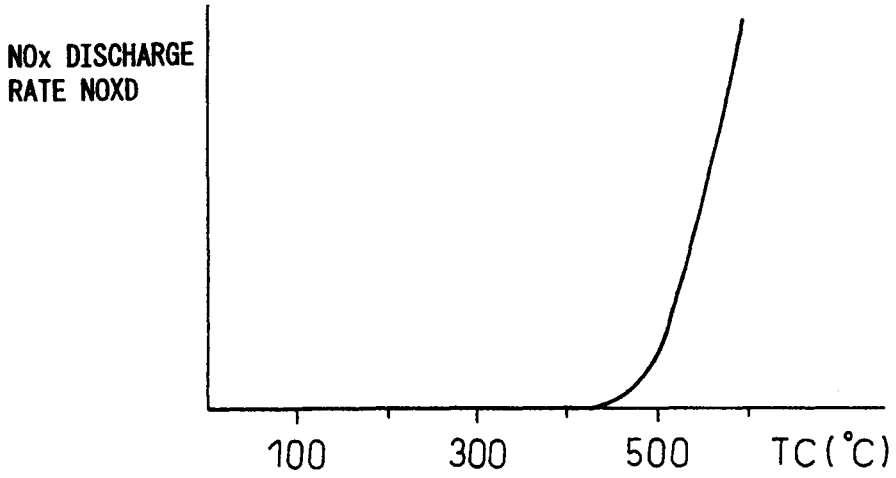


Fig.13

(A)


NOx DISCHARGE
RATE NOXD
100
300
500
TC(°C)

(B)

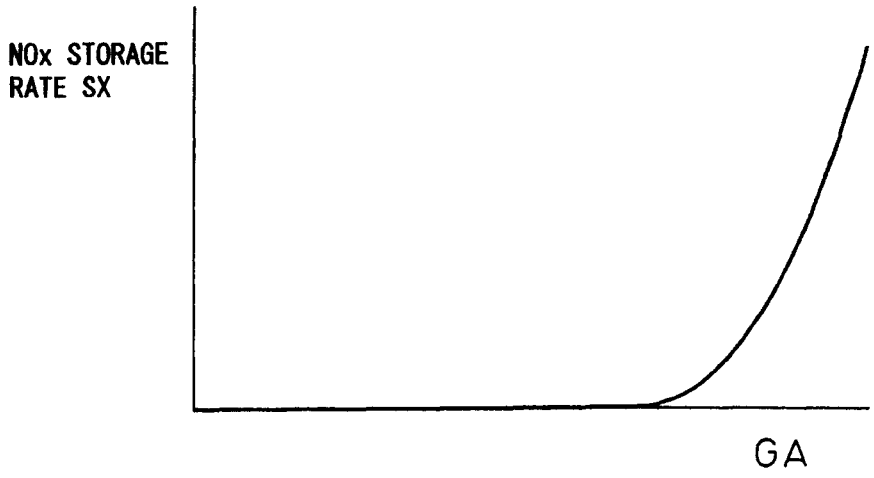

NOx STORAGE
RATE SX
GA

Fig.14

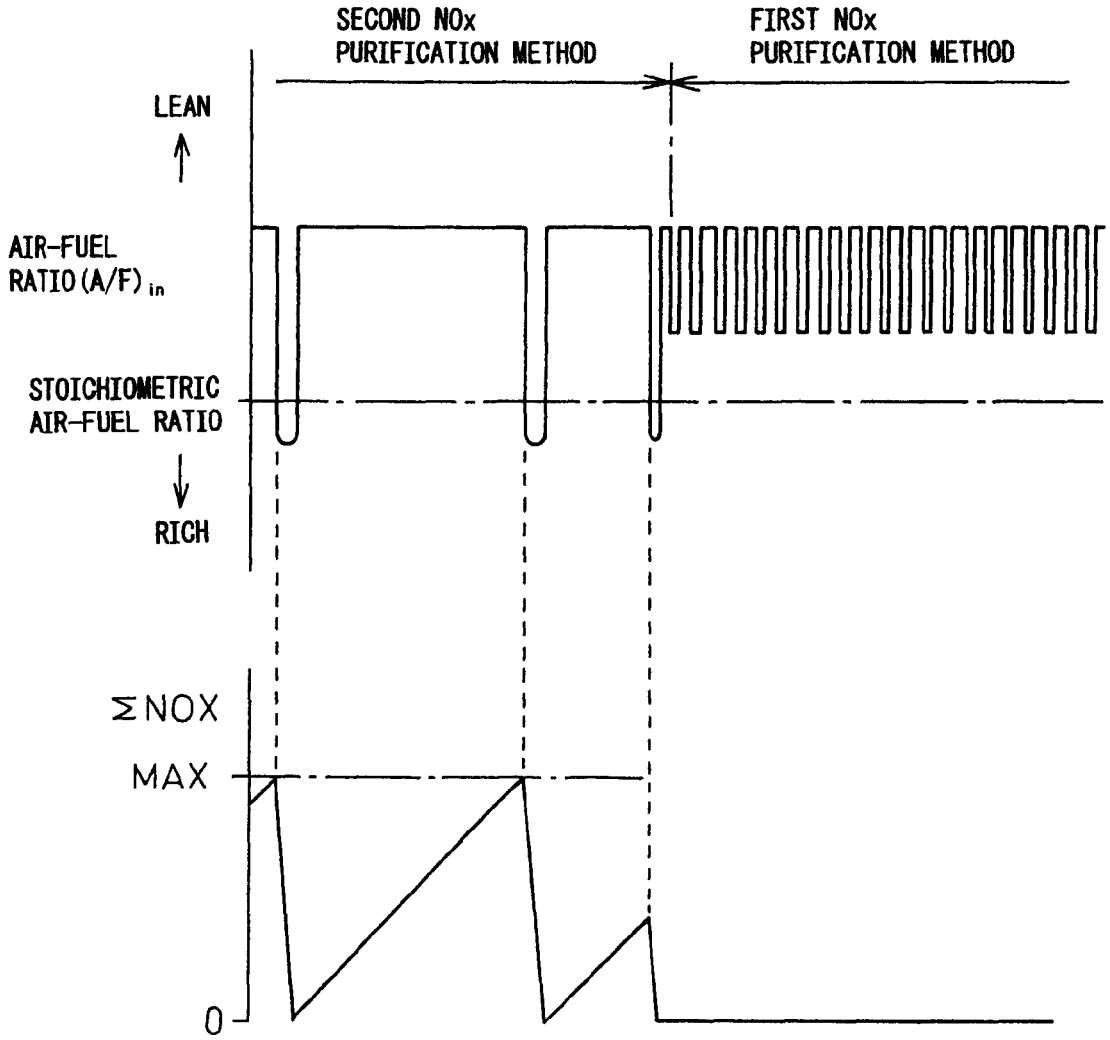

SECOND NOx PURIFICATION METHOD
FIRST NOx PURIFICATION METHOD
LEAN
AIR-FUEL RATIO (A/F) in
STOICHIOMETRIC AIR-FUEL RATIO
RICH
ΣNOX
MAX
0

Fig.15

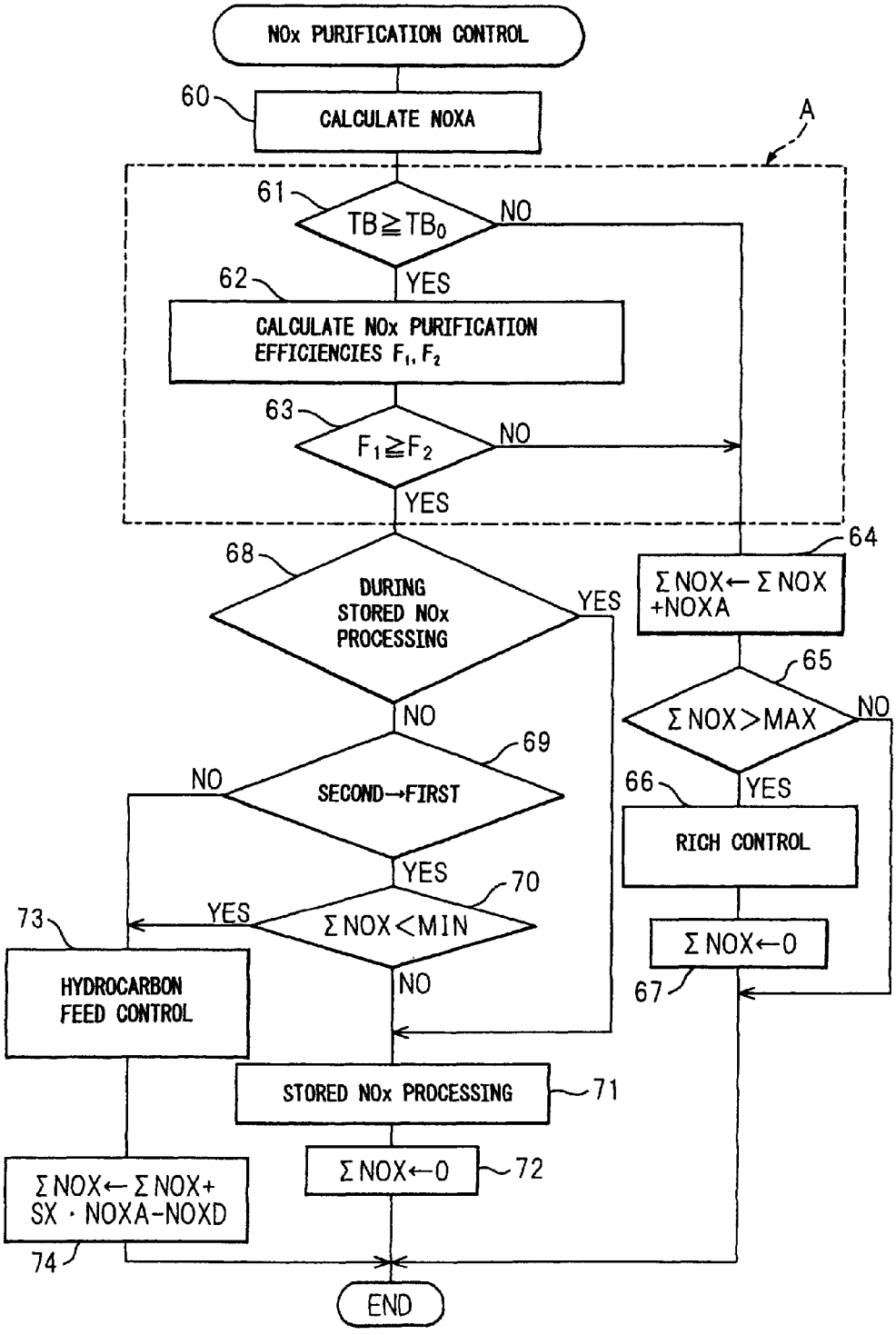
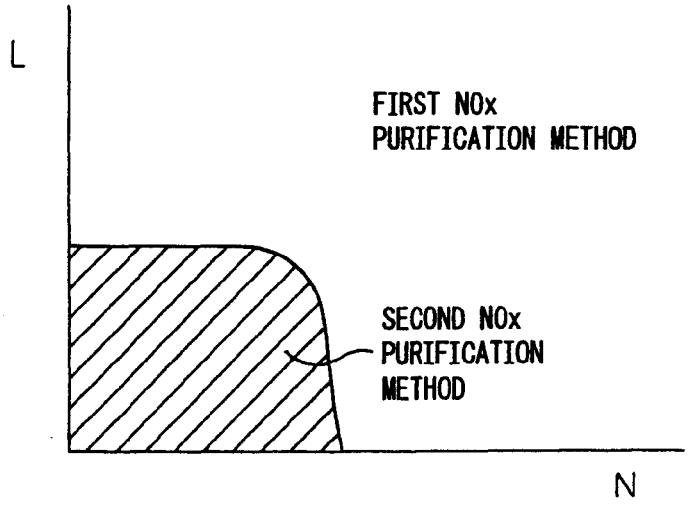

NOx PURIFICATION CONTROL
60
CALCULATE NOXA
A
61
TB≧TB0
NO
YES
62
CALCULATE NOx PURIFICATION EFFICIENCIES F1, F2
63
F1≧F2
NO
YES
64
ΣNOX←ΣNOX +NOXA
65
ΣNOX>MAX
NO
YES
66
RICH CONTROL
ΣNOX←0
67
68
DURING STORED NOx PROCESSING
YES
NO
69
SECOND→FIRST
NO
YES
70
ΣNOX<MIN
YES
NO
73
HYDROCARBON FEED CONTROL
STORED NOx PROCESSING
71
ΣNOX←0
72
ΣNOX←ΣNOX+ SX · NOXA-NOXD
74
END

Fig.16

(A)


L
FIRST NOx
PURIFICATION METHOD
SECOND NOx
PURIFICATION
METHOD
N

(B)

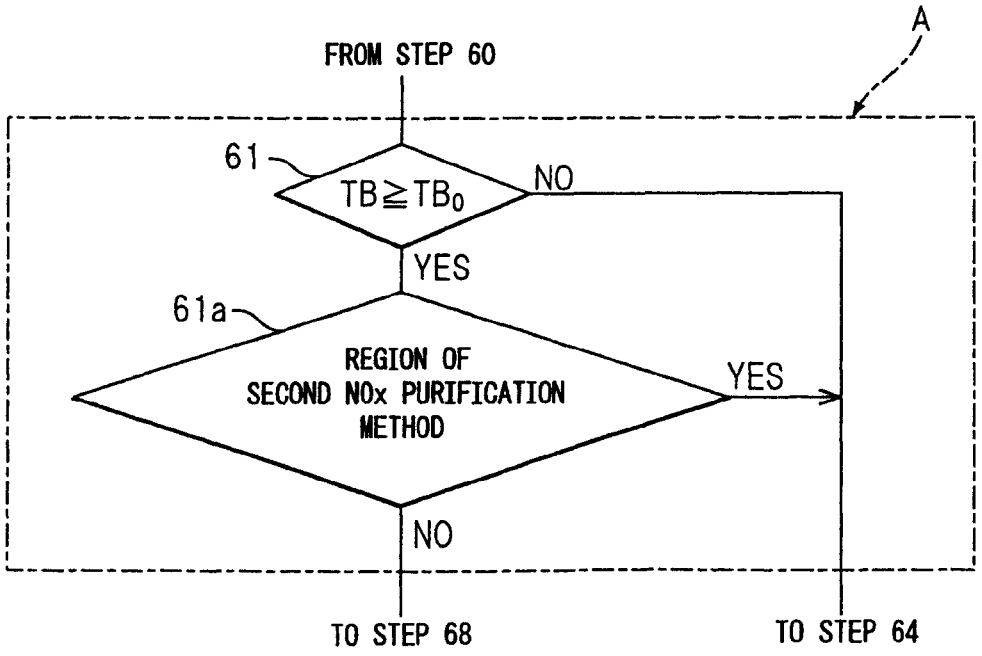

A
FROM STEP 60
61
TB≧TB0
NO
YES
61a
REGION OF
SECOND NOx PURIFICATION
METHOD
YES
NO
TO STEP 68
TO STEP 64

Fig.17

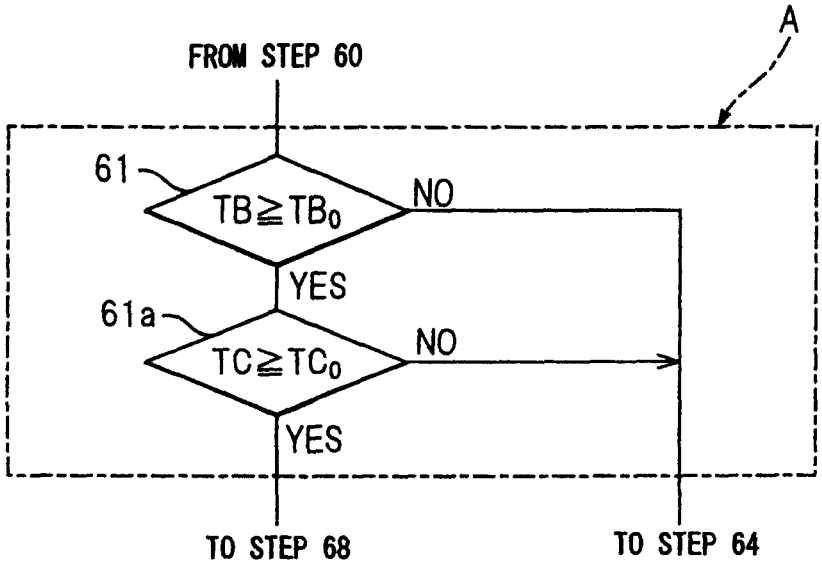

A
FROM STEP 60
61
TB≧TB0
NO
YES
61a
TC≧TC0
NO
YES
TO STEP 68
TO STEP 64

Fig.18

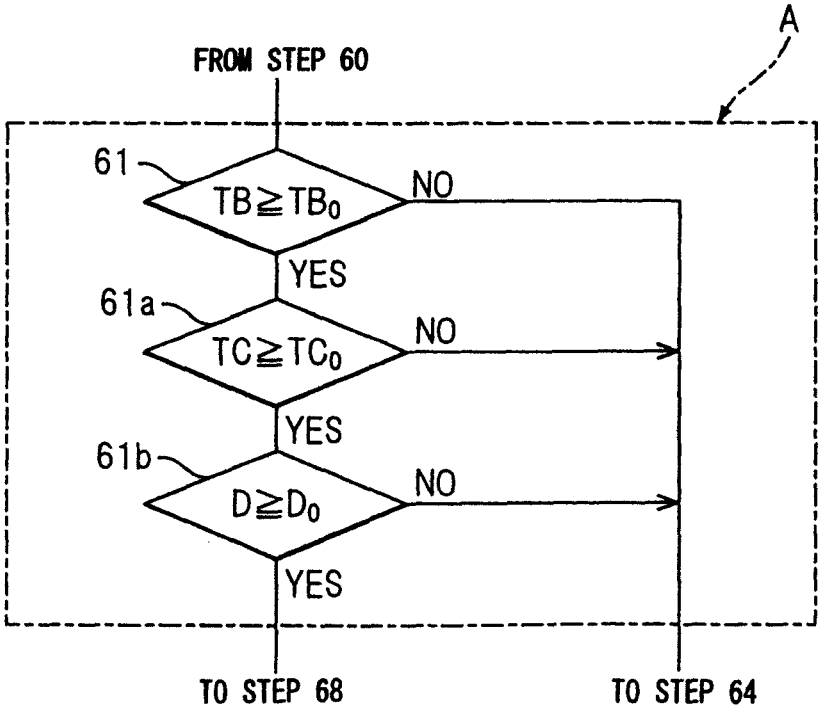

A
FROM STEP 60
61
TB≧TB0
NO
YES
61a
TC≧TC0
NO
YES
61b
D≧D0
NO
YES
TO STEP 68
TO STEP 64

Fig.19

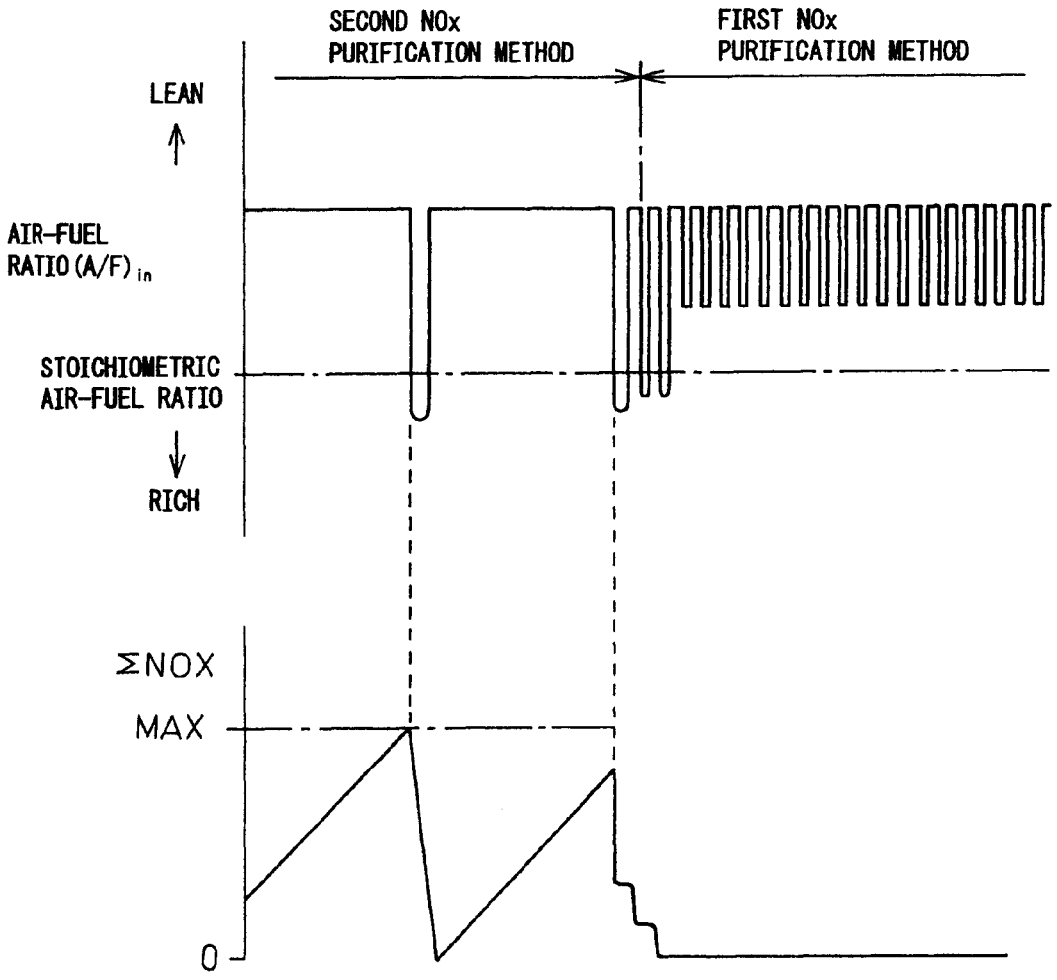

SECOND NOx
PURIFICATION METHOD
FIRST NOx
PURIFICATION METHOD
LEAN
AIR-FUEL
RATIO (A/F) in
STOICHIOMETRIC
AIR-FUEL RATIO
RICH
ΣNOX
MAX
0

Fig.20

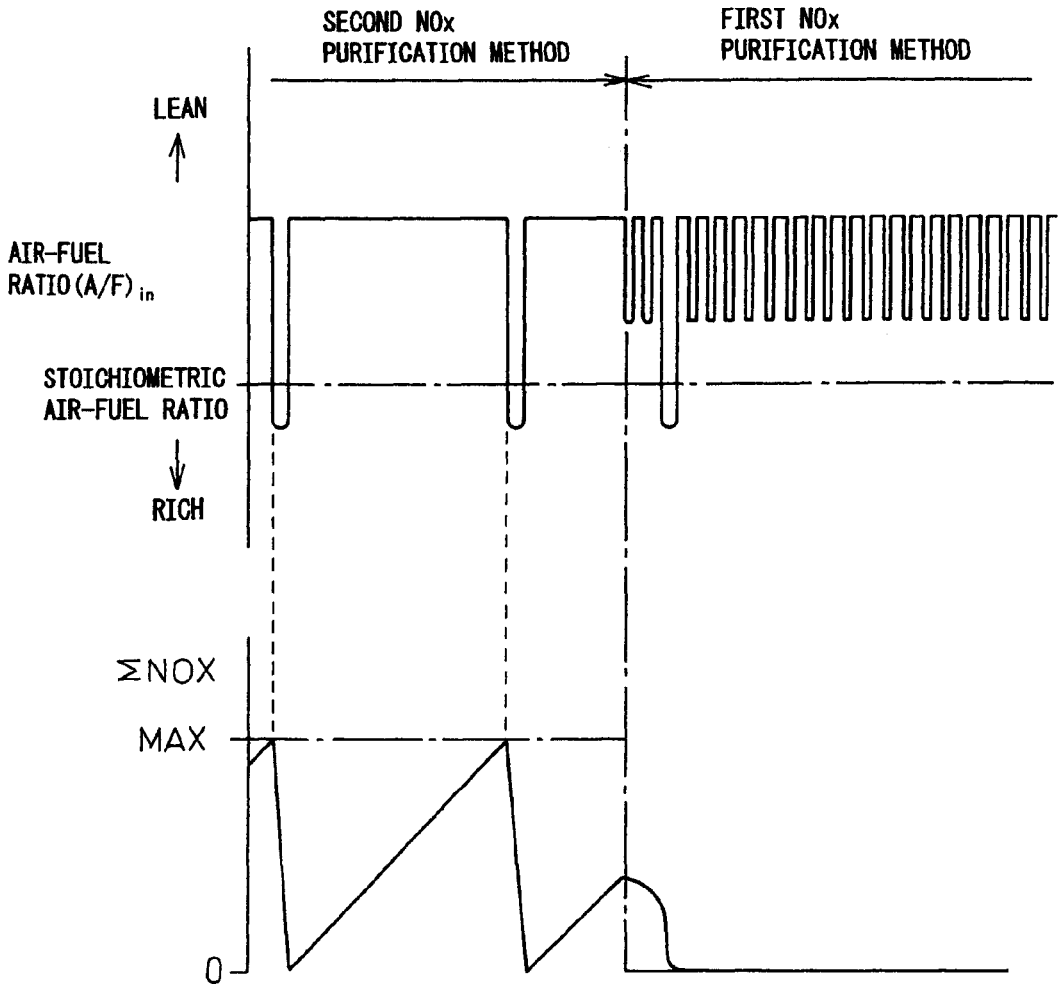

SECOND NOx
PURIFICATION METHOD
FIRST NOx
PURIFICATION METHOD
LEAN
AIR-FUEL
RATIO (A/F) in
STOICHIOMETRIC
AIR-FUEL RATIO
RICH
ΣNOX
MAX
0

Fig.21

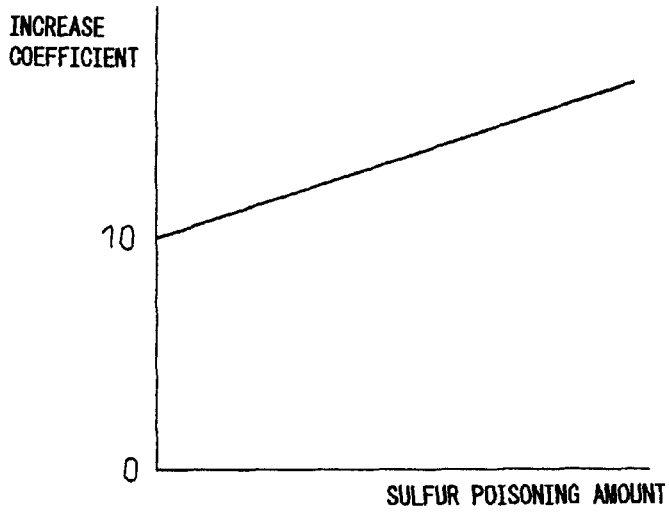
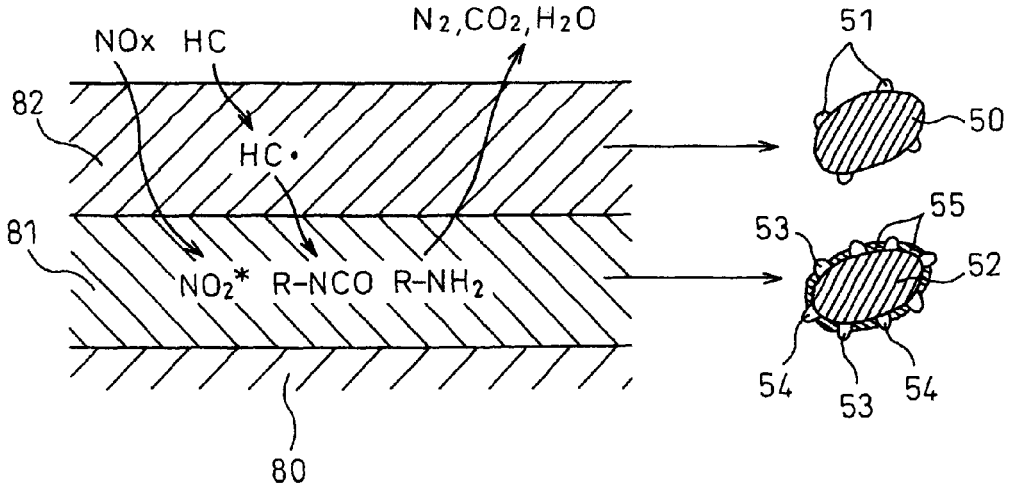

INCREASE
COEFFICIENT
10
0
SULFUR POISONING AMOUNT

Fig.22


NOx HC
N2,CO2,H2O
82
HC•
81
NO2* R-NCO R-NH2
80
51
50
55
53
52
54
53
54

EXHAUST PURIFICATION SYSTEM OF INTERNAL COMBUSTION ENGINE

CONTINUATION INFORMATION

This is a Continuation of application Ser. No. 13/202,733 filed Sep. 30, 2011, which in turn is a National Stage Application of PCT/JP2010/054740 filed Mar. 15, 2010. The disclosure of the prior applications is hereby incorporated by reference herein in its entirety.

TECHNICAL FIELD

The present invention relates to an exhaust purification system of an internal combustion engine.

BACKGROUND ART

Known in the art is an internal combustion engine which arranges, in an engine exhaust passage, an NO_x storage catalyst which stores NO_x which is contained in exhaust gas when the air-fuel ratio of the inflowing exhaust gas is lean and which releases the stored NO_x, when the air-fuel ratio of the inflowing exhaust gas becomes rich, which arranges, in the engine exhaust passage upstream of the NO_x storage catalyst, an oxidation catalyst which has an adsorption function, and which feeds hydrocarbons into the engine exhaust passage upstream of the oxidation catalyst to make the air-fuel ratio of the exhaust gas flowing into the NO_x storage catalyst rich when releasing NO_x from the NO_x storage catalyst (for example, see Patent Literature 1).

In this internal combustion engine, the hydrocarbons which are fed when releasing NO_x from the NO_x storage catalyst are made gaseous hydrocarbons at the oxidation catalyst, and the gaseous hydrocarbons are fed to the NO_x storage catalyst. As a result, the NO_x which is released from the NO_x storage catalyst is reduced well.

CITATION LIST

Patent Literature

Patent Literature 1: Japanese Patent No. 3969450

SUMMARY OF INVENTION

Technical Problem

However, there is the problem that when the NO_x storage catalyst becomes a high temperature, the NO_x purification rate falls.

An object of the present invention is to provide an exhaust purification system of an internal combustion engine which can obtain a high NO_x purification rate even if the temperature of the exhaust purification catalyst becomes a high temperature.

Solution to Problem

According to the present invention, there is provided an exhaust purification system of an internal combustion engine wherein a hydrocarbon feed valve for feeding hydrocarbons is arranged inside an engine exhaust passage, an exhaust purification catalyst for reacting NO_x contained in exhaust gas and hydrocarbons which are injected from the hydrocarbon feed valve and are partially oxidized is arranged in the engine exhaust passage downstream of the hydrocarbon feed valve, a precious metal catalyst is carried on the exhaust purification catalyst and a basic layer is formed on the exhaust purification catalyst, the exhaust purification catalyst has a property of reducing the NO_X which is contained in the exhaust gas when hydrocarbons are injected from the hydrocarbon feed valve at predetermined feed intervals while maintaining an air-fuel ratio of an exhaust gas flowing into the exhaust purification catalyst lean and has a property of being increased in storage amount of NO_X which is contained in the exhaust gas when the feed intervals of the hydrocarbons are longer than the predetermined feed intervals, and, at the time of engine operation, a first NO_X purification method which injects hydrocarbons from the hydrocarbon feed valve at the predetermined feed intervals while maintaining the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst lean so as to remove the NO_X contained in the exhaust gas and a second NO_X purification method which switches the air-fuel ratio of the exhaust gas which flows to the exhaust purification catalyst from lean to rich by intervals longer than the predetermined feed intervals so as to remove the NO_X are selectively used in accordance with an operating state of an engine.

Advantageous Effects of Invention

By selectively using the first NO_X purification method and the second NO_X purification method, it is possible to obtain a high NO_X purification rate regardless of the operating state of the engine.

BRIEF DESCRIPTION OF DRAWINGS

FIG. **1** is an overall view of a compression ignition type internal combustion engine.

FIG. **2** is a view schematically showing a surface part of a catalyst carrier.

FIG. **3** is a view for explaining an oxidation reaction in an oxidation catalyst.

FIG. **4** is a view showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. **5** is a view showing an NO_x purification rate.

FIG. **6** is view for explaining an oxidation reduction reaction in an exhaust purification catalyst.

FIG. **7** is a view for explaining an oxidation reduction reaction in an exhaust purification catalyst.

FIG. **8** is a view showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst etc.

FIG. **9** is a view showing a map of an exhausted NO_X amount NOXA.

FIG. **10** is a view showing a fuel injection timing.

FIG. **11** is a view showing an NO_X purification rate.

FIG. **12** is a view showing a map of a hydrocarbon injection amount.

FIG. **13** is a view showing an NO_X discharge rate etc.

FIG. **14** is a view showing a change in an air-fuel ratio of exhaust gas (A/F) in etc. when switching from a second NO_X purification method to a first NO_X purification method.

FIG. **15** is a flow chart for NO_X purification control.

FIG. **16** is a view showing a flow chart etc. showing another embodiment of an NO_X purification method determining part A shown in FIG. **15**.

FIG. **17** is a view showing a flow chart etc. showing still another embodiment of an NO_X purification method determining part A shown in FIG. **15**.

FIG. **18** is a view showing a flow chart etc. showing another embodiment of an NO_X purification method determining part A shown in FIG. **15**.

FIG. **19** is a timing chart showing a change in an air-fuel ratio of exhaust gas (A/F) in etc. when switching from a second NO_X purification method to a first NO_X purification method.

FIG. **20** is a timing chart showing a change in an air-fuel ratio of exhaust gas (A/F) in etc. when switching from a second NO_X purification method to a first NO_X purification method.

FIG. **21** is a view showing an increase coefficient.

FIG. **22** is a partial enlarged cross-sectional view of another catalyst for removing NO_X.

DESCRIPTION OF EMBODIMENTS

FIG. **1** is an overall view of a compression ignition type internal combustion engine.

Referring to FIG. **1**, **1** indicates an engine body, **2** a combustion chamber of each cylinder, **3** an electronically controlled fuel injector for injecting fuel into each combustion chamber **2**, **4** an intake manifold, and **5** an exhaust manifold. The intake manifold **4** is connected through an intake duct **6** to an outlet of a compressor **7***a* of an exhaust turbocharger **7**, while an inlet of the compressor **7***a* is connected through an intake air amount detector **8** to an air cleaner **9**. Inside the intake duct **6**, a throttle valve **10** driven by a step motor is arranged. Furthermore, around the intake duct **6**, a cooling device **11** is arranged for cooling the intake air which flows through the inside of the intake duct **6**. In the embodiment shown in FIG. **1**, the engine cooling water is guided to the inside of the cooling device **11** where the engine cooling water is used to cool the intake air.

On the other hand, the exhaust manifold **5** is connected to an inlet of the exhaust turbine **7***b* of the exhaust turbocharger **7**, while the outlet of the exhaust turbine **7***b* is connected through an exhaust pipe **12** to an inlet of a hydrocarbon partial oxidation catalyst **13** able to partially oxidize the hydrocarbons HC. In the embodiment shown in FIG. **1**, this hydrocarbon partial oxidation catalyst **13** is comprised of an oxidation catalyst. An outlet of the hydrocarbon partial oxidation catalyst, that is, the oxidation catalyst **13**, is connected to an inlet of an exhaust purification catalyst **14**, while an outlet of the exhaust purification catalyst **14** is connected to a particulate filter **15** for trapping particulate which is contained in the exhaust gas. Inside of the exhaust pipe **12** upstream of the oxidation catalyst **13**, a hydrocarbon feed valve **16** is arranged for feeding hydrocarbons comprised of diesel oil or other fuel used as fuel of a compression ignition type internal combustion engine. In the embodiment shown in FIG. **1**, diesel oil is used as the hydrocarbons which are fed from the hydrocarbon feed valve **16**. Note that, the present invention can also be applied to a spark ignition type internal combustion engine which burns fuel under a lean air-fuel ratio. In this case, hydrocarbons comprised of gasoline or other fuel which is used as fuel of a spark ignition type internal combustion engine are fed from the hydrocarbon feed valve **16**.

On the other hand, the exhaust manifold **5** and the intake manifold **4** are connected with each other through an exhaust gas recirculation (hereinafter referred to as an "EGR") passage **17**. Inside the EGR passage **17**, a electronically controlled EGR control valve **18** is arranged. Further, around the EGR passage **17**, a cooling device **19** is arranged for cooling EGR gas flowing through the inside of the EGR passage **17**. In the embodiment shown in FIG. **1**, the engine cooling water is guided to the inside of the cooling device **19** where the engine cooling water is used to cool the EGR gas. On the other hand, each fuel injector **3** is connected through a fuel feed tube **20** to a common rail **21**. This common rail **21** is connected through an electronically controlled variable discharge fuel pump **22** to a fuel tank **23**. The fuel which is stored inside of the fuel tank **23** is fed by the fuel pump **22** to the inside of the common rail **21**. The fuel which is fed to the inside of the common rail **21** is fed through each fuel feed tube **20** to the fuel injector **3**.

An electronic control unit **30** is comprised of a digital computer provided with a ROM (read only memory) **32**, a RAM (random access memory) **33**, a CPU (microprocessor) **34**, an input port **35**, and an output port **36**, which are connected with each other by a bidirectional bus **31**. At the oxidation catalyst **13**, a temperature sensor **24** is attached for detecting the temperature of the oxidation catalyst **13**. At the exhaust purification catalyst **14**, a temperature sensor **25** is attached for detecting the temperature of the exhaust purification catalyst **14**. The output signals of these temperature sensors **24** and **25** and intake air amount detector **8** are input through corresponding AD converters **37** to the input port **35**. Further, the accelerator pedal **40** has a load sensor **41** connected to it which generates an output voltage proportional to the amount of depression L of the accelerator pedal **40**. The output voltage of the load sensor **41** is input through a corresponding AD converter **37** to the input port **35**. Furthermore, at the input port **35**, a crank angle sensor **42** is connected which generates an output pulse every time a crankshaft rotates by, for example, 15°. On the other hand, the output port **36** is connected through corresponding drive circuits **38** to each fuel injector **3**, a step motor for driving the throttle valve **10**, the hydrocarbon feed valve **16**, the EGR control valve **18**, and the fuel pump **22**.

FIG. **2**(A) schematically shows a surface part of a catalyst carrier carried on a substrate of an oxidation catalyst **13**. As shown in FIG. **2**(A), for example, a catalyst **51** comprised of platinum Pt or another such precious metal or silver Ag or copper Cu or other such transition metal is carried on a catalyst carrier **50** comprised of alumina.

On the other hand, FIG. **2**(B) schematically shows a surface part of a catalyst carrier which is carried on a substrate of the exhaust purification catalyst **14**. At this exhaust purification catalyst **14**, as shown in FIG. **2**(B), for example, there is provided a catalyst carrier **52** made of alumina on which precious metal catalysts **53** and **54** are carried. Furthermore, on this catalyst carrier **52**, a basic layer **55** is formed which includes at least one element selected from potassium K, sodium Na, cesium Cs, or another such alkali metal, barium Ba, calcium Ca, or another such alkali earth metal, a lanthanoid or another such rare earth and silver Ag, copper Cu, iron Fe, iridium Ir, or another metal able to donate electrons to NO_x. The exhaust gas flows along the top of the catalyst carrier **53**, so the precious metal catalysts **53** and **54** can be said to be carried on the exhaust gas flow surface of the exhaust purification catalyst **14**. Further, the surface of the basic layer **55** exhibits basicity, so the surface of the basic layer **55** is called the basic exhaust gas flow surface part **56**.

In FIG. **2**(B), the precious metal catalyst **53** is comprised of platinum Pt, while the precious metal catalyst **54** is comprised of rhodium Rh. That is, the precious metal catalysts **53** and **54** which are carried on the catalyst carrier **52** are comprised of platinum Pt and rhodium Rh. Note that, on the catalyst carrier **52** of the exhaust purification catalyst **14**, in addition to platinum Pt and rhodium Rh, palladium Pd may be further carried or, instead of rhodium Rh, palladium

Pd may be carried. That is, the precious metal catalysts **53** and **54** which are carried on the catalyst carrier **52** are comprised of platinum Pt and at least one of rhodium Rh and palladium Pd.

When hydrocarbons are injected from the hydrocarbon feed valve **16** into the exhaust gas, the hydrocarbons are oxidized on the oxidation catalyst **13**. In the present invention, at this time, the hydrocarbons are partially oxidized at the oxidation catalyst **13** and the partially oxidized hydrocarbons are used to remove the NO_X at the exhaust purification catalyst **14**. In this case, if making the oxidizing strength of the oxidation catalyst **13** too strong, the hydrocarbons end up being oxidized without being partially oxidized at the oxidation catalyst **13**. To make the hydrocarbons partially oxidize, it is necessary to weaken the oxidizing strength of the oxidation catalyst **13**. Therefore, in an embodiment of the present invention, as an oxidation catalyst **13**, a catalyst with a little carried amount of the precious metal catalyst, a catalyst carrying a base metal, or a catalyst with a small volume is used.

FIG. **3** schematically shows an oxidation reaction which is performed in the oxidation catalyst **13**. As shown in FIG. **3**, the hydrocarbons HC which are injected from the hydrocarbon feed valve **16** become radical hydrocarbons HC with a small carbon number due to the catalyst **51**. Note that, at this time, part of the hydrocarbons HC bond with the NO to become nitroso compounds such as shown in FIG. **3**, while part of the hydrocarbons HC bond with NO_2 to form nitro compounds. These radical hydrocarbons etc. produced at the oxidation catalyst **13** are sent to the exhaust purification catalyst **14**.

Next, referring to FIG. **4** to FIG. **6**, a first NO_X purification method discovered by the inventors will be explained.

Note that, FIG. **4** shows the change in the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst **14**, while FIG. **5** shows the NO_X purification rate by the exhaust purification catalyst **14** with respect to the catalyst temperatures TC of the exhaust purification catalyst **14** when changing the air-fuel ratio (A/F) in of the exhaust gas flowing to the exhaust purification catalyst **14** as shown in FIG. **4**.

Now, the inventors engaged in repeated research on NO_X purification over a long period of time and, in the process of research, learned that, as shown in FIG. **4**, if intermittently lowering the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst **14** by later explained certain time intervals within a range of a lean air-fuel ratio, an extremely high NO_X purification rate is obtained even in a 400° C. or more high temperature region as shown in FIG. **5**. Furthermore, it was learned that, at this time, a large amount of a reducing intermediate containing nitrogen and hydrocarbons continues to be held or adsorbed on the surface of the basic layer **55**, that is, on the basic exhaust gas flow surface part **56** of the exhaust purification catalyst **14**, and this reducing intermediate plays a central role in obtaining a high NO_X purification rate.

Next, this will be explained with reference to FIGS. **6**(A) and **6**(B). Note that, these FIGS. **6**(A) and **6**(B) schematically show the surface part of the catalyst carrier **52** of the exhaust purification catalyst **14**. These FIGS. **6**(A) and **6**(B) show the reaction which is presumed to occur when the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst **14** is intermittently reduced within the range of a lean air-fuel ratio as shown in FIG. **4**.

That is, as will be understood from FIG. **4**, the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst **14** is maintained lean, so the exhaust gas which flows into the exhaust purification catalyst **14** becomes a state of oxygen excess. Therefore, the NO which is contained in the exhaust gas, as shown in FIG. **6**(A), is oxidized on the platinum **53** and becomes NO_2. Next, this NO_2 is further oxidized and becomes stable nitrate ions NO_3^-.

On the other hand, when nitrates NO_3^- are produced, the nitrates NO_3^- are pulled back in a direction of reduction by the hydrocarbons HC which are sent on to the surface of the basic layer **55**, have the oxygen disassociated, and becomes unstable NO_2*. This unstable NO_2* is strong in activity. Below, this unstable NO_2^- is called the active NO_2*. This active NO_2*, as shown in FIG. **6**(A), reacts with the mainly radical hydrocarbons HC which are adhered on the surface of the basic layer **55** or on the rhodium Rh **54** or with the mainly radical hydrocarbons HC contained in the exhaust gas on the rhodium Rh **54**, whereby a reducing intermediate is produced. This reducing intermediate is adhered or adsorbed on the surface of the basic layer **55**.

Note that, at this time, the first produced reducing intermediate is believed to be a nitro compound R—NO_2. If this nitro compound R—NO_2 is produced, the result becomes a nitrile compound R—CN, but this nitrile compound R—CN can only survive for an instant in this state, so immediately becomes an isocyanate compound R—NCO. This isocyanate compound R—NCO, when hydrolyzed, becomes an amine compound R—NH_2. However, in this case, what is hydrolyzed is considered to be part of the isocyanate compound R—NCO. Therefore, as shown in FIG. **6**(A), the majority of the reducing intermediate which is held or adsorbed on the surface of the basic layer **55** is believed to be the isocyanate compound R—NCO and amine compound R—NH_2.

On the other hand, as shown in FIG. **6**(B), the active NO_2* reacts with the reducing intermediate R—NCO or R—NH_2 on the rhodium Rh **54** to form N_2, CO_2, and H_2O and consequently the NO_x is removed. That is, if no reducing intermediate R—NCO or R—NH_2 is held or adsorbed on the basic layer **55**, the NO_X is not removed. Therefore, to obtain a high NO_X purification rate, it is necessary to ensure the continuous presence of a sufficient amount of the reducing intermediate R—NCO or R—NH_2 for making the active NO_2* N_2, CO_2, and H_2O on the basic layer **55**, that is, the basic exhaust gas flow surface part **26**, at all times.

That is, as shown in FIGS. **6**(A) and **6**(B), to oxidize the NO on the platinum Pt 53, the air-fuel ratio (A/F) in of the exhaust gas must be lean. It is necessary to hold a sufficient amount of the reducing intermediate R—NCO or R—NH_2 for making the produced active NO_2* N_2, CO_2, and H_2O on the surface of the basic layer **55**, that is, it is necessary to provide the basic exhaust gas flow surface part **26** for holding the reducing intermediate R—NCO or R—NH_2.

Therefore, as shown in FIGS. **6**(A) and **6**(B), to react the NO_X contained in the exhaust gas and the partially oxidized hydrocarbons and produce a reducing intermediate R—NCO or R—NH_2 containing nitrogen and hydrocarbon, precious metal catalysts **53** and **54** are carried on the exhaust gas flow surface of the exhaust purification catalyst **14**, a basic exhaust gas flow surface part **26** is formed around the precious metal catalysts **53** and **54** to hold the produced reducing intermediate R—NCO or R—NH_2 in the exhaust purification catalyst **14**, and the NO_X is reduced by the reducing action of the reducing intermediate R—NCO or R—NH_2 held on the basic exhaust gas flow surface part **26**. Therefore, in this first NO_X purification method, hydrocarbons HC are intermittently fed from the hydrocarbon feed valve **16** by predetermined feed intervals while maintaining the air-fuel ratio of the exhaust gas flowing into the exhaust

purification catalyst **14** lean. The predetermined feed intervals of the hydrocarbons HC are made the feed interval required for continuing to ensure the presence of the reducing intermediate R—NCO or R—NH_2 on the basic exhaust gas flow surface part **56**.

In this case, if the injection amount becomes too large or the injection interval becomes too short, the amount of hydrocarbons becomes excessive and a large amount of hydrocarbons HC is exhausted from the exhaust purification catalyst **14**, while if the injection amount becomes too small or the injection interval becomes too long, the reducing intermediate R—NCO or R—NH_2 can no longer remain on the basic exhaust gas flow surface part **56**. Therefore, in this case, what is important is setting the injection amount and injection interval of hydrocarbons so that so that no excess hydrocarbons HC are exhausted from the exhaust purification catalyst **14** and so that the reducing intermediate R—NCO or the R—NH_2 continues on the basic exhaust gas flow surface part **26**. Incidentally, in the example shown in FIG. **4**, the injection interval is made 3 seconds.

Next, while referring to FIG. **7** to FIG. **11**, the second NO_X purification method will be explained. In the case shown in FIG. **4**, if making the feed intervals of the hydrocarbons HC longer than the above-mentioned predetermined feed intervals, the hydrocarbons HC and the reducing intermediate R—NCO or R—NH_2 disappear from the surface of the basic layer **55**. At this time, no pullback force in a direction, which reduces nitrate ions NO_3^-, acts on the nitrate ions NO_3^- produced on the platinum Pt 53. Therefore, at this time, the nitrate ions NO_3^- diffuse in the basic layer **55** and becomes nitrates as shown in FIG. **7**(A). That is, at this time, the NO_X in the exhaust gas is absorbed in the form of nitrates inside the basic layer **55**.

On the other hand, FIG. **7**(B) shows the case where the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **14** is made the stoichiometric air-fuel ratio or rich when the NO_x is absorbed in the form of nitrates inside of the basic layer **55**. In this case, the oxygen concentration in the exhaust gas falls, so the reaction proceeds in the opposite direction ($NO_3^- \rightarrow NO_2$) and consequently the nitrates absorbed in the basic layer **55** become nitrate ions NO_3^- one by one and, as shown in FIG. **7**(B), are released from the basic layer **55** in the form of NO_2. Next, the released NO_2 is reduced by the hydrocarbons HC and CO contained in the exhaust gas.

FIG. **8** shows a second NO_X purification method utilizing the adsorption and release action of NO_X. That is, in this second NO_X purification method, as shown in FIG. **8**, when the stored NO_X amount ΣNOX which is stored in the basic layer **55** exceeds a predetermined allowable amount MAX, the air-fuel ratio (A/F) in of the exhaust gas which flows into the exhaust purification catalyst **14** is temporarily made rich. If the air-fuel ratio (A/F) in of the exhaust gas is made rich, the NO_X which was absorbed at the basic layer **55** when the air-fuel ratio (A/F) in of the exhaust gas was lean, is released all at once from the basic layer **55** and reduced. Due to this, the NO_X is removed.

The stored NO_X amount ΣNOX is, for example, calculated from the NO_X amount which is exhausted from the engine. In an embodiment of the present invention, the exhausted NO_X amount NOXA which is exhausted from the engine per unit time is stored as a function of the engine load L and engine speed N in the form of a map such as shown in FIG. **9** in advance in the ROM **32**. The stored NO_X amount ΣNOX is calculated from this exhausted NO_X amount NOXA. The period by which the air-fuel ratio (A/F) in of the exhaust gas is made rich is far longer than the period by which the air-fuel ratio (A/F) in of the exhaust gas is lowered, as shown in FIG. **4**, and the period by which the air-fuel ratio (A/F) in of the exhaust gas is made rich is usually 1 minute or more.

In the second NO_X purification method, when the air-fuel ratio (A/F) in of the exhaust gas is lean, the NO_X which is contained in the exhaust gas is absorbed in the basic layer **55**. Therefore, the basic layer **55** performs the role of an absorbent for temporarily absorbing NO_X. Note that, at this time, sometimes the basic layer **55** temporarily adsorbs the NO_x. Therefore, if using term of storage as a term including both absorption and adsorption, at this time, the basic layer **55** performs the role of an NO_x storage agent for temporarily storing the NO_x. That is, if the ratio of the air and fuel (hydrocarbons) which are fed into the engine intake passage, combustion chambers **2**, and exhaust passage upstream of the exhaust purification catalyst **14** is called the air-fuel ratio of the exhaust gas, in this second NO_X purification method, the exhaust purification catalyst **14** functions as an NO_x storage catalyst which stores the NO_x when the air-fuel ratio of the exhaust gas is lean and releases the stored NO_x when the oxygen concentration in the exhaust gas falls.

Further, in this second NO_X purification method, as shown in FIG. **10**, in addition to the combustion use fuel M from the fuel injector **3**, additional fuel W is injected into the combustion chamber **2** whereby the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst **14** is made rich. Note that, the abscissa of FIG. **10** shows the crank angle. This additional fuel W is injected at a timing where it is burned, but does not appear as engine output, that is, slightly before ATDC90° after compression top dead center. Of course, in this case, it is also possible to make the feed amount of hydrocarbons from the hydrocarbon feed valve **16** increase so as to make the air-fuel ratio (A/F) in of the exhaust gas rich.

FIG. **11** shows the NO_x purification rate when making the exhaust purification catalyst **14** function as an NO_x storage catalyst. Note that, the abscissa of the FIG. **11** shows the catalyst temperature TC of the exhaust purification catalyst **14**. When making the exhaust purification catalyst **14** function as an NO_x storage catalyst, as shown in FIG. **11**, when the catalyst temperature TC is 300° C. to 400° C., an extremely high NO_x purification rate is obtained, but when the catalyst temperature TC becomes a 400° C. or higher high temperature, the NO_x purification rate falls.

In this way, when the catalyst temperature TC becomes 400° C. or more, the NO_x purification rate falls because if the catalyst temperature TC becomes 400° C. or more, the nitrates break down by heat and are released in the form of NO_2 from the exhaust purification catalyst **14**. That is, so long as storing NO_x in the form of nitrates, when the catalyst temperature TC is high, it is difficult to obtain a high NO_x purification rate. However, in the first NO_x purification method shown from FIG. **4** to FIGS. **6**(A) and **6**(B), as will be understood from FIGS. **6**(A) and **6**(B), nitrates are not formed or even if formed are extremely fine in amount, consequently, as shown in FIG. **5**, even when the catalyst temperature TC is high, a high NO_x purification rate is obtained.

That is, the first NO_x purification method shown from FIG. **4** to FIGS. **6**(A) and **6**(B) can be said to be a new NO_x purification method which removes NO_X without formation of almost any nitrates when using an exhaust purification catalyst which carries a precious metal catalyst and forms a basic layer which can absorb NO_X. In actuality, when using this first NO_x purification method, the nitrates which are

detected from the basic layer **53** become much smaller in amount compared with the case of using the second NO_X purification method.

On the other hand, to use the first NO_X purification method to remove NO_X, it is necessary to feed a certain amount or more of hydrocarbons by a short period even when the NO_X concentration in the exhaust gas is low. Therefore, when the NO_X concentration of the exhaust gas is low, the NO_X purification efficiency deteriorates. As opposed to this, in the second NO_X purification method, when the NO_X concentration in the exhaust gas is low, the time until the stored NO_X amount ΣNOX reaches the allowable value MAX becomes longer, and thus the period for making the air-fuel ratio (A/F) in of the exhaust gas rich become longer. Accordingly, the NO_X purification efficiency does not become poor. Therefore, when the NO_X concentration in the exhaust gas is low, it can be said to be preferable to use the second NO_X purification method rather than the first NO_X purification method.

That is, which of the first NO_X purification method and the second NO_X purification method should be used changes in the operating state of the engine. Therefore, in the present invention, on the exhaust purification catalyst **14**, precious metal catalysts **53** and **54** are carried and a basic layer **55** is formed, and the exhaust purification catalyst **14** has the property of reducing the NO_x which is contained in the exhaust gas when hydrocarbons are injected from the hydrocarbon feed valve **16** at predetermined feed intervals while maintaining the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst **14** is maintained lean and has the property of being increased in the storage amount of NO_X which is contained in exhaust gas when the feed intervals of the hydrocarbons are made longer than the predetermined feed intervals. At the time of engine operation, a first NO_X purification method which injects hydrocarbons from the hydrocarbon feed valve **16** at the predetermined feed intervals while maintaining the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst **14** lean so as to remove the NO_X contained in the exhaust gas and a second NO_X purification method which switches the air-fuel ratio of the exhaust gas which flows to the exhaust purification catalyst **14** from lean to rich by intervals longer than the predetermined feed intervals so as to remove the NO_X are selectively used in accordance with the operating state of the engine.

Next, referring to FIG. **12** to FIG. **15**, a representative embodiment according to the present invention will be explained.

FIG. **12**(A) shows the hydrocarbon feed amount QE from the hydrocarbon feed valve **16**, while FIG. **12**(B) shows the additional fuel amount W which is fed into a combustion chamber **2**. The hydrocarbon feed amount QE is stored as a function of the engine load QE and engine speed N in the form of a map such as shown in FIG. **12**(A) in advance in the ROM **32**. The additional fuel amount W is also stored as a function of the engine load QE and engine speed N in the form of a map such as shown in FIG. **12**(B) in advance in the ROM **32**.

FIG. **13**(A) shows a discharge rate NOXD of stored NO_X which is discharged from the exhaust purification catalyst **14** when the air-fuel ratio (A/F) in of the exhaust gas is lean. As explained above, the NO_X which is stored in the form of nitrates is broken down by heat and discharged if the temperature TC of the exhaust purification catalyst **14** rises. At this time, the NO_X discharge rate NOXD, that is, the NO_X amount NOXD which is discharged per unit time, rapidly rises when the temperature TC of the exhaust purification catalyst **14** exceeds the heat breakdown start temperature of about 450° C.

On the other hand, FIG. **13**(B) shows the storage rate SX of the NO_X which is stored in the exhaust purification catalyst **14** when the first NO_X purification method is used to perform the purification action of NO_X. When the first NO_X purification method is used to perform the purification action of NO_X, normally NO_X is not stored in the exhaust purification catalyst **14**. However, if the flow rate of the exhaust gas becomes faster, that is, if the intake air amount GA increases, the reaction time becomes shorter and the reaction can no longer be sufficiently performed, so active NO_2* is not formed and the NO_X which is absorbed at the basic layer **55** increases. Therefore, as shown in FIG. **13**(B), when the intake air amount GA becomes larger than a certain value, the NO_X storage rate SX starts to increase.

In this way, even when the first NO_X purification method is used to perform an NO_X purification action, sometimes NO_X is stored in the exhaust purification catalyst **14**. At this time, the amount of NO_X stored per unit time becomes the value SX·NOXA of the NO_X storage rate SX multiplied with the NO_X amount NOXA exhausted per unit time. In an embodiment of the present invention, SX·NOXA is cumulatively added to calculate the stored NO_X amount which is stored when the first NO_x purification method is used to perform the NO_X purification action. When switched from the first NO_X purification method to the second NO_X purification method, the stored NO_X amount which is calculated at the time of the first NO_X purification method is used as the basis to start to calculate the stored NO_X amount.

That is, in a representative example according to the present invention, when switched from the first NO_X purification method to the second NO_X purification method, the NO_X storage amount which was calculated when the first NO_X purification method is used and the NO_X storage amount which was calculated after switching to the second NO_X purification method are totaled up. When this total value ΣNOX exceeds a predetermined allowable value MAX, the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst **14** is made temporarily rich. In this case, if ignoring the stored NO_X amount of the time when using the first NO_X purification method, the timing at which the air-fuel ratio (A/F) in of the exhaust gas is made rich when switched to the second NO_X purification method becomes slower and consequently part of the NO_X is exhausted into the atmosphere without being stored. However in an embodiment of the present invention, the NO_X storage amount of the time when the first NO_X purification method is used is taken into consideration. Therefore, the above such problem does not arise.

On the other hand, when switched from the second NO_X purification method to the first NO_X purification method, if stored NO_X remains in the exhaust purification catalyst **14**, the stored NO_X is discharged from the NO_X purification catalyst **14** when the temperature TC of the exhaust purification catalyst **14** is caused to rise due to the feed of hydrocarbons. When an NO_X purification action is performed by the first NO_X purification method, no reducing action is performed on the thus discharged NO_X, consequently the NO_x is exhausted into the atmosphere.

However, if making the air-fuel ratio (A/F) in of the exhaust gas rich, it is possible to reduce the stored NO_X which remained in the exhaust purification catalyst **14** and consequently possible to block the NO_X from being exhausted into the atmosphere. Therefore, in an embodiment of the present invention, as shown in FIG. **14**, when

switched from the second NO_X purification method to the first NO_X purification method, the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **14** is temporarily made rich to release and reduce the NO_X which was stored in the exhaust purification catalyst **14**.

In this case, in the embodiment shown in FIG. **14**, right before being switched from the second NO_X purification method to the first NO_X purification method, additional fuel W is fed into the combustion chamber **2** whereby the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst **14** is made rich. Note that, FIG. **14** shows the change of the air-fuel ratio (A/F) in of the exhaust gas which flows into the exhaust purification catalyst **14** and the stored NO_X amount ΣNOX which is stored in the exhaust purification catalyst **14**. As will be understood from FIG. **14**, when the first NO_X purification method is started, the stored NO_X amount ΣNOX becomes zero and consequently NO_X is kept from being exhausted into the atmosphere.

On the other hand, the NO_X purification action by the first NO_X purification method is not performed so long as the oxidation catalyst **13** is not activated. Therefore, in an embodiment of the present invention, the first NO_X purification method is used only when the temperature TB of the oxidation catalyst **13** becomes the activation temperature TB_0 or more. When the temperature TB of the oxidation catalyst **13** is lower than the activation temperature TB_0, use of the first NO_X purification method is prohibited. At this time, that is, when the temperature TB of the oxidation catalyst **13** is lower than the activation temperature TB_0, the second NO_X purification method is used.

Note that, in a representative embodiment of the present invention, when the temperature TB of the oxidation catalyst **13** is the activation temperature TB_0 or more, either of the first NO_X purification method or the second NO_X purification method is used. In this case, when using the first NO_X purification method would result in a higher NO_X purification efficiency compared with using the second NO_X purification method, the first NO_X purification method is used, while when using the second NO_X purification method would result in a higher NO_X purification efficiency compared with using the first NO_X purification method, the second NO_X purification method is used.

FIG. **15** shows the NO_X purification control routine for executing the representative embodiment of the present invention. This routine is executed by interruption every predetermined time interval.

Referring to FIG. **15**, first, at step **60**, the NO_X amount NOXA exhaust per unit time is calculated from the map shown in FIG. **9**. Next, the routine proceeds to an NO_X purification method determining part A for determining whether to use the first NO_X purification method or use the second NO_X purification method. With this NO_X purification method determination part A, first, at step **61**, it is judged if the temperature TB of the oxidation catalyst **13** is the activation temperature TB_0 or more. When $TB<TB_0$, it is judged that the second NO_X purification method should be used. At this time, the routine proceeds to step **64**.

As opposed to this, when $TB \geq TB_0$, the routine proceeds to step **62** where the NO_X purification efficiency F_1 when using the first NO_X purification method and the NO_X purification efficiency F_2 when using the second NO_X purification method are calculated. The NO_X purification efficiencies F_1 and F_2 express the amounts of consumption of fuel or hydrocarbons per unit time required for obtaining a unit NO_X purification rate. In this case, the NO_X purification efficiency F_1 is calculated from the hydrocarbon feed amount QE and hydrocarbon injection interval shown in FIG. **12**A and the NO_X purification rate shown in FIG. **5**, while the NO_X purification efficiency F_2 is calculated from the additional fuel amount W shown in FIG. **12**B, the interval between timings where the rich air-fuel ratio is set in FIG. **8**, and the NO_X purification rate shown in FIG. **11**.

Next, at step **63**, it is judged if the NO_X purification efficiency F_1 is higher than the NO_X purification efficiency F_2. When $F_1 \geq F_2$, it is judged that the first NO_X purification method should be used. At this time, the routine proceeds to step **68**. As opposed to this, when $F_1<F_2$, it is judged that the second NO_X purification method should be used, and the routine proceeds to step **64**.

Next, the second NO_X purification method which is performed from step **64** to step **67** will be explained. First, at step **64**, the exhausted NO_X amount NOXA shown in FIG. **9** is added to ΣNOX to calculate the stored NO_X amount ΣNOX. Next, at step **65**, it is judged if the stored NO_X amount ΣNOX exceeds the allowable value MAX. When ΣNOX>MAX, the routine proceeds to step **66** where the additional fuel amount W is calculated from the map shown in FIG. **12**B, then the additional fuel injection action is performed. Next, at step **67**, ΣNOX is cleared.

Next, the first NO_X purification method which is performed from step **68** to step **74** will be explained. First, at step **68**, it is judged if stored NO_X processing is being performed for processing the stored NO_X remaining inside the exhaust purification catalyst **14**. When stored NO_X processing is not being performed, the routine proceeds to step **69** where it is judged if a decision to switch from the second NO_X purification method to the first NO_X purification method has now been made. If a decision to switch from the second NO_X purification method to the first NO_X purification method has now been made, the routine proceeds to step **70** where it is judged if the stored NO_X amount ΣNOX is smaller than a predetermined small value MIN.

When ΣNOX>MIN, the routine proceeds to step **71** where stored NO_X processing is performed. In this embodiment, as shown in FIG. **14**, right before being switched from the second NO_X purification method to the first NO_X purification method, the air-fuel ratio (A/F) in of the exhaust gas is temporarily made rich. Next, at step **72**, ΣNOX is cleared. Note that, when the stored NO_X processing has started, the routine jumps from step **68** to step **71** until the stored NO_X processing is completed.

On the other hand, when it is judged at step **69** that a decision to switch from the second NO_X purification method to the first NO_X purification method has not now been made, the routine proceeds to step **73**. Further, when it is judged at step **70** that ΣNOX<MIN, that is, even when it is judged that almost no NO_X is stored, the routine proceeds to step **73**. At step **73**, the hydrocarbon feed amount QE is calculated from the map such as shown in FIG. **12**(A), so hydrocarbon injection processing is performed. Next, at step **74**, the following formula is used as the basis to calculate the NO_X amount ΣNOX which is stored in the exhaust purification catalyst **14** during an NO_X purification action by the first NO_X purification method.

$$\Sigma NOX \leftarrow \Sigma NOX + SX \cdot NOXA - NOXD$$

where, SX·NOXA, as explained above, is the NO_X amount which is stored per unit time and NOXD is the discharge rate shown in FIG. **13**A. When switched from the first NO_X purification method to the second NO_X purification method, at step **64**, NOXA is added to the ΣNOX calculated at step **74**.

FIG. **16** shows another embodiment. In this embodiment, the engine operating region where the NO_X purification efficiency F_2 becomes higher than the NO_X purification efficiency F_1 is set in advance as shown by the hatching in FIG. **16**(A), for example, as a function of the engine load L and engine speed N. When the oxidation catalyst **13** is activated, the NO_X purification method is determined in accordance with FIG. **16**(A).

FIG. **16**(B) shows another embodiment of the NO_X purification method determining part A of FIG. **15**. Referring to FIG. **16**(B), at step **61**, when the temperature TB of the oxidation catalyst **13** is lower than the activation temperature TB_0, it is judged that the second NO_X purification method should be used, then the routine proceeds to step **64** of FIG. **15**. As opposed to this, when it is judged at step **61** that $TB \geq TB_0$, the routine proceeds to step **61***a* where it is judged if the operating state of the engine is a region shown by the hatching in FIG. **16**(A) where the second NO_X purification method should be used. When the operating state of the engine is a region where the second NO_X purification method should be used, the routine proceeds to step **64** of FIG. **15**. As opposed to this, when it is judged that the operating state of the engine is not a region where the second NO_X purification method should be used, the routine proceeds to step **68** of FIG. **15**.

FIG. **17** shows still another embodiment of the NO_X purification method determining part A of FIG. **15**. That is, the NO_X purification rate when using the first NO_X purification method, as shown in FIG. **5**, is rapidly lowered when the temperature TC of the exhaust purification catalyst **14** becomes the limit temperature TC_0 or less. As opposed to this, as shown in FIG. **11**, the NO_X purification rate when using the second NO_X purification method falls relatively slowly when the temperature TC of the exhaust purification catalyst **14** falls. Therefore, in this embodiment, when the temperature TC of the exhaust purification catalyst **14** is higher than the limit temperature TC_0, the first NO_X purification method is used, while when the temperature TC of the exhaust purification catalyst **14** is lower than the limit temperature TC_0, the second NO_X purification method is used.

That is, referring to FIG. **17**, at step **61**, when the temperature TB of the oxidation catalyst **13** is lower than the activation temperature TB_0, it is judged that the second NO_X purification method should be used then the routine proceeds to step **64** of FIG. **15**. As opposed to this, when it is judged at step **61** that $TB \geq TB_0$, the routine proceeds to step **61***a* where it is judged if the temperature TC of the exhaust purification catalyst **14** is higher than the limit temperature TC_0. When $TC < T_0$, the routine proceeds to step **64** of FIG. **15**. As opposed to this, when $TC \geq T_0$, it is judged that the first NO_X purification method should be used then the routine proceeds to step **68** of FIG. **15**.

FIG. **18** shows still another embodiment of the NO_X purification method determining part A of FIG. **15**. That is, the first NO_X purification method can give a high NO_X purification rate as compared with the second NO_X purification method when the NO_X amount to be reduced is large, that is, when the NO_X concentration in the exhaust gas is high. Therefore, in this embodiment, it is judged whether to use the first NO_X purification method or to use the second NO_X purification method by whether the NO_X concentration D in the exhaust gas exceeds a set value D_0.

That is, referring to FIG. **18**, at step **61**, when the temperature TB of the oxidation catalyst **13** is lower than the activation temperature TB_0, it is judged that the second NO_X purification method should be used, then the routine proceeds to step **64** of FIG. **15**. As opposed to this, when it is judged at step **61** that $TB \geq TB_0$, the routine proceeds to step **61***a* where it is judged if the temperature TC of the exhaust purification catalyst **14** is higher than the limit temperature TC_0. When $TC < T_0$, the routine proceeds to step **64** of FIG. **15**. As opposed to this, when $TC \geq T_0$, the routine proceeds to step **61***b* where it is judged if the NO_X concentration D in the exhaust gas which is detected by for example, the NO_X concentration sensor is higher than the set value D_0. When $D < D_0$, the routine proceeds to step **64** of FIG. **15**. As opposed to this, when $D \geq D_0$, it is judged that the first NO_X purification method should be used, then the routine proceeds to step **68** of FIG. **15**.

FIG. **19** shows another embodiment of the stored NO_X processing which is performed at step **71** of FIG. **15**. In this embodiment, right after being switched from the second NO_X purification method to the first NO_X purification method as well, the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst **14** is made rich. At this time, the amount of hydrocarbons which is fed from the hydrocarbon feed valve **16** is increased so that the air-fuel ratio (A/F) in of the exhaust gas is made rich.

That is, when a decision has been made to switch from the second NO_X purification method to the first NO_X purification method, if the stored NO_X amount ΣNOX is large, if just injecting additional fuel to the inside of the combustion chamber **2** so as to make air-fuel ratio (A/F) in of the exhaust gas rich just once, sometimes it is not possible to release the total stored NO_X for reduction. In such a case, as shown in FIG. **19**, when the NO_X purification action by the first NO_X purification method is started, by increasing the feed amount of hydrocarbons, the air-fuel ratio (A/F) in of the exhaust gas is made rich whereby the total stored NO_X is released and reduced.

On the other hand, if injecting additional fuel into the combustion chamber **2**, the temperature inside the combustion chamber **2** rises. Therefore, at the time of a high load operation where the combustion temperature becomes higher, sometimes the air-fuel ratio (A/F) in of the exhaust gas cannot be made rich by injecting the additional fuel into the combustion chamber **2**. In such a case, the air-fuel ratio (A/F) in of the exhaust gas is made rich by stopping the injection of the additional fuel and increasing the feed amount of hydrocarbons.

FIG. **20** shows still another embodiment of the stored NO_X processing which is performed at step **71** of FIG. **15**. In this embodiment, after being switched from the second NO_X purification method to the first NO_X purification method, the NO_X purification action is started by the first NO_X purification method, then the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst **14** is made rich. In this embodiment, when the stored NO_X is discharged from the exhaust purification catalyst **14**, this discharged NO_X is reduced by feeding additional fuel to the combustion chamber **2** or increasing the feed amount of hydrocarbons to make the air-fuel ratio (A/F) in of the exhaust gas rich.

On the other hand, if the sulfur which is contained in the exhaust gas sticks to the surface of the precious metal, that is, if the precious metal is poisoned by sulfur, active NO_2* becomes harder to produce. Therefore, it is preferable to increase the feed amount of hydrocarbons QE as the sulfur poisoning amount of the precious metal is increased so that the amount of production of active NO_2* does not fall even if the precious metal is poisoned by sulfur. In the embodiment shown in FIG. **21**, the increase coefficient for the hydrocarbon feed amount QE is increased along with the increase in the sulfur poisoning amount so that the amount

of production of active NO_2* does not fall even if the sulfur poisoning amount is increased.

FIG. **22** shows the case of forming the hydrocarbon partial oxidation catalyst **13** and the exhaust purification catalyst **14** shown in FIG. **1** by a single catalyst. This catalyst is for example provided with a large number of exhaust gas channels extending in the direction of flow of the exhaust gas. FIG. **22** shows an enlarged cross-sectional view of the surface part of the inner circumferential wall **80** of an exhaust gas channel of the catalyst. As shown in FIG. **22**, on the surface of the inner circumferential wall **80** of the exhaust gas channel, a bottom coat layer **81** is formed. On this bottom coat layer **81**, a top coat layer **82** is formed. In the example shown in FIG. **22**, both the coat layers **81** and **82** are comprised of powder aggregates. FIG. **22** shows enlarged views of the powder forming the coat layers **81** and **82**. From the enlarged views of the powder, it is learned that the top coat layer **82** is comprised of the hydrocarbon partial oxidation catalyst shown in FIG. **2**(A), for example, an oxidation catalyst, while the bottom coat layer **81** is comprised of the exhaust purification catalyst shown in FIG. **2**(B).

When the catalyst shown in FIG. **22** is used, as shown in FIG. **22**, the hydrocarbons HC which are contained in the exhaust gas diffuse inside the top coat layer **82** and are partially oxidized. The partially oxidized hydrocarbons diffuse inside the bottom coat layer **81**. That is, in the example shown in FIG. **22** as well, in the same way as the example shown in FIG. **1**, the hydrocarbon partial oxidation catalyst and the exhaust purification catalyst are arranged so that the hydrocarbons which were partially oxidized at the hydrocarbon partial oxidation catalyst flow to the exhaust purification catalyst. On the other hand, in the catalyst shown in FIG. **22**, when the first NO_X purification method is used, the NO_X which is contained in the exhaust gas diffuses to the inside of the bottom coat layer **81** and becomes active NO_2*. At this time, at the bottom coat layer **81**, the reducing intermediate R—NCO or R—NH_2 is produced from the active NO_2* and the partially oxidized hydrocarbons. Furthermore, the active NO_2* reacts with the reducing intermediate R—HCO or R—NH_2 to become N_2, CO_2, and H_2O.

On the other hand, as shown in FIG. **2**(B), on the catalyst carrier **52** of the exhaust purification catalyst **14**, precious metals **53** and **54** are carried. Therefore, inside of the exhaust purification catalyst **14** as well, it is possible to reform the hydrocarbons to radical hydrocarbons HC with a small carbon number. In this case, if the hydrocarbons can be sufficiently reformed inside the exhaust purification catalyst **14**, that is, if the hydrocarbons can be sufficiently partially oxidized inside of the exhaust purification catalyst **14**, it is not necessary to arrange the oxidation catalyst **13** as shown in FIG. **1** upstream of the exhaust purification catalyst **14**. Therefore, in an embodiment according to the present invention, no oxidation catalyst **13** is attached inside of the engine exhaust passage. Therefore, in this embodiment, the hydrocarbons which are injected from the hydrocarbon feed valve **16** are directly fed to the exhaust purification catalyst **14**.

In this embodiment, the hydrocarbons which are injected from the hydrocarbon feed valve **16** are partially oxidized inside of the exhaust purification catalyst **14**. Furthermore, inside of the exhaust purification catalyst **14**, active NO_2* is produced from the NO_X which is contained in the exhaust gas. Inside of the exhaust purification catalyst **14**, the reducing intermediate R—NCO and R—NH_2 is produced from these active NO_2* and partially oxidized hydrocarbons. Furthermore, the active NO_2* reacts with the reducing intermediate R—NCO or R—NH_2 to become N_2, CO_2, and H_2O. That is, in this embodiment, the exhaust purification catalyst **14** for reacting the hydrocarbons injected from the hydrocarbon feed valve **16** and partially oxidized and the NO_X contained in the exhaust gas is arranged inside of the engine exhaust passage downstream of the hydrocarbon feed valve **16**.

REFERENCE SIGNS LIST

4 . . . intake manifold
5 . . . exhaust manifold
7 . . . exhaust turbocharger
12 . . . exhaust pipe
13 . . . oxidation catalyst
14 . . . exhaust purification catalyst
16 . . . hydrocarbon feed valve

What is claimed is:

1. A method of purifying NO_X contained in exhaust gas, the method comprising a first NO_X purification method and a second NO_X purification method, wherein the first NO_X purification method and the second NO_X purification method comprise:

supplying exhaust gas containing NO_X to an exhaust gas passage;

injecting hydrocarbons in the exhaust gas passage at predetermined feed intervals to form a mixture with the exhaust gas containing NO_X;

feeding the exhaust gas or the mixture to an exhaust purification catalyst; and

reducing the NO_X contained in the exhaust gas, wherein

a precious metal catalyst is carried on the exhaust purification catalyst,

a basic layer is formed on the exhaust purification catalyst,

a hydrocarbon feed valve injects the hydrocarbons in the exhaust gas passage, wherein

in the first method, the injected hydrocarbons are partially oxidized, and an air-fuel ratio of the exhaust gas and an air-fuel ratio of the mixture flowing into the exhaust purification catalyst is lean, thereby, the exhaust purification catalyst chemically reduces NO_X contained in the exhaust gas without storing nitrates, or with storing a fine amount of nitrates, in the basic layer formed on the exhaust purification catalyst, and the first method further comprises:

reacting the NO_X and the partially oxidized hydrocarbons contained in the mixture at the precious metal catalyst to produce a reducing intermediate containing nitrogen and hydrocarbons;

holding the produced reducing intermediate on the basic layer; and

chemically reducing the NO_X contained in the exhaust gas by a reducing action of the reducing intermediate held on the basic layer, thereby chemically reducing the NO_X contained in the exhaust gas without storing nitrates, or with storing a fine amount of nitrates, in the basic layer formed on the exhaust purification catalyst, and

in the second method, the injection of the hydrocarbons from the hydrocarbon feed valve occurs at intervals longer than the predetermined feed intervals in the first method, wherein

when the feed intervals of the hydrocarbons are longer than the predetermined feed intervals of the first method, the exhaust purification catalyst

increases in a storage amount of NO_X, thereby physically reducing the NO_X contained in the exhaust gas, and

when the feed intervals of the hydrocarbons are longer than the predetermined feed intervals of the first method, and when an air-fuel ratio of the mixture is switched from lean to rich, NO_X is chemically reduced, and

at the time of engine operation, the first NO_X purification method and the second NO_X purification method are selectively performed in accordance with an operating state of an engine.

2. The method of claim **1**, wherein inside of the engine exhaust passage and downstream of the hydrocarbon feed valve,

a hydrocarbon partial oxidation catalyst partially oxidizes the hydrocarbons in the mixture, and

the exhaust purification catalyst and the hydrocarbon partial oxidation catalyst are arranged so that the hydrocarbons that are partially oxidized at the hydrocarbon partial oxidation catalyst flow into the exhaust purification catalyst.

3. The method of claim **2**, wherein the hydrocarbon partial oxidation catalyst is comprised of an oxidation catalyst which is arranged inside of the engine exhaust passage upstream of the exhaust purification catalyst.

4. The method of claim **2**, wherein a top coat layer comprised of the hydrocarbon partial oxidation catalyst is formed on a bottom coat layer comprised of the exhaust purification catalyst.

5. The method of claim **2**, wherein in the first NO_X purification method,

the predetermined feed intervals of the hydrocarbons are the feed intervals necessary for a continued presence of the reducing intermediate on a basic exhaust gas flow surface part.

6. The method of claim **1**, wherein in the first NO_X purification method,

the predetermined feed intervals of the hydrocarbons are the feed intervals necessary for a continued presence of the reducing intermediate on a basic exhaust gas flow surface part.

7. The method of claim **1**, wherein in the second NO_X purification method, when the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst is lean, NO_X in the exhaust gas is absorbed in the basic layer and, when the air-fuel ratio of the mixture flowing into the exhaust purification catalyst becomes rich, the absorbed NO_X is released from the basic layer and chemically reduced.

8. The method of claim **1**, wherein the precious metal catalyst is comprised of platinum Pt and at least one of rhodium Rh and palladium Pd.

9. The method of claim **1**, wherein the basic layer includes an alkali metal, alkali earth metal, rare earth, or metal able to donate electrons to NO_X.

10. The method of claim **1**, wherein the first NO_X purification method is only performed when a temperature of an oxidation catalyst becomes an activation temperature or more and wherein performance of the first NO_X purification method is prohibited when the temperature of the oxidation catalyst is lower than the activation temperature.

11. The method of claim **10**, wherein either the first NO_X purification method or the second NO_X purification method is performed when a temperature of the oxidation catalyst is the activation temperature or more.

12. The method of claim **11**, the method further comprising:

comparing a NO_X purification efficiency of the first and second method, and

if performing the first NO_X purification method would result in a higher NO_X purification efficiency compared to performing the second NO_X purification method, the first NO_X purification method is performed, or

if performing the second NO_X purification method would result in a higher NO_X purification efficiency compared to performing the first NO_X purification method, the second NO_X purification method is performed.

13. The method of claim **11**, wherein when the NO_X purification rate starts to be lowered when a temperature of the exhaust purification catalyst becomes a limit temperature or less, when the temperature of the exhaust purification catalyst is higher than the limit temperature, the first NO_X purification method is performed, and when the temperature of the exhaust purification catalyst is lower than the limit temperature, the second NO_X purification method is performed.

14. The method of claim **10**, wherein the second NO_X purification method is performed when a temperature of the oxidation catalyst is lower than the activation temperature.

15. The method of claim **1**, wherein when switched from the second NO_X purification method to the first NO_X purification method, the air-fuel ratio of the mixture flowing into the exhaust purification catalyst is temporarily made rich to release and chemically reduce the NO_X that is stored in the exhaust purification catalyst.

16. The method claim **15**, wherein directly before being switched from the second NO_X purification method to the first NO_X purification method, the air-fuel ratio of the mixture flowing into the exhaust purification catalyst is made rich.

17. The method of claim **16**, wherein directly after being switched from the second NO_X purification method to the first NO_X purification method, the air-fuel ratio of the mixture flowing into the exhaust purification catalyst is made rich.

18. The method of claim **15**, wherein after being switched from the second NO_X purification method to the first NO_X purification method, the NO_X purification action is started by the first NO_X purification method, then the air-fuel ratio of the mixture flowing into the exhaust purification catalyst is made rich.

19. The method of claim **1**, wherein the first and second method further comprise:

calculating the amount of NO_X stored in the exhaust purification catalyst, wherein

when the calculated amount of NO_X stored in the exhaust purification catalyst exceeds a predetermined allowable value, the air-fuel ratio of the mixture flowing into the exhaust purification catalyst is temporarily made rich, and

when switched from the first NO_X purification method to the second NO_X purification method, the NO_X storage amount calculated when the first NO_X purification method is performed and the NO_X storage amount calculated after switching to the second NO_X purification method are totaled up and, when a total value exceeds a predetermined allowable value, the

air-fuel ratio of the mixture flowing into the exhaust purification catalyst is made temporarily rich.

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